



Adsorption — from theory to practice[☆]

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Abstract

Adsorption at various interfaces has concerned scientists since the beginning of this century. This phenomenon underlies a number of extremely important processes of utilitarian significance. The technological, environmental and biological importance of adsorption can never be in doubt. Its practical applications in industry and environmental protection are of paramount importance. The adsorption of substrates is the first stage in many catalytic processes. The methods for separation of mixtures on a laboratory and on an industrial scale are increasingly based on utilising the change in concentration of components at the interface. Moreover, such vital problems as purification of water, sewage, air and soil are involved here too. On the other hand, many areas in which technological innovation has covered adsorption phenomena have been expanded more through art and craft than through science. A basic understanding of the scientific principles is far behind; in part because the study of interfaces requires extremely careful experimentation if meaningful and reproducible results are to be obtained. In recent years, however, considerable effort has been increasingly directed toward closing the gap between theory and practice. Crucial progress in theoretical description of the adsorption has been achieved, mainly through the development of new theoretical approaches formulated on a molecular level, by means of computer simulation methods and owing to new techniques which examine surface layers or interfacial regions. Moreover, during the last 15 years new classes of solid adsorbents have been developed, such as activated carbon fibres and carbon molecular sieves, fullerenes and heterofullerenes, microporous glasses and nanoporous — both carbonaceous and inorganic — materials. Nanostructured solids are very popular in science and technology and have gained extreme interest due to their sorption, catalytic, magnetic, optical and thermal properties. Although the development of adsorption up to the 1918s has been following

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rather a zig-zag path, this arm of surface science is now generally considered to have become a well-defined branch of physical science representing an intrinsically interdisciplinary area between chemistry, physics, biology and engineering. This review presents in brief the history of adsorption and highlights the progress in theoretical description of the phenomenon under consideration. The paper deals with the above problems critically, showing the development of adsorption, presenting some of the latest important results and giving a source of up-to-date literature on it. Moreover, in this paper the most important aspects are overviewed referring to today's trends and visions in application of adsorption science in industry, environmental protection and in environmental analysis. *The relationship between development of adsorption theory and adsorption practice is pointed out.* Current understanding and perspectives pertaining to applications of adsorption phenomena on laboratory and on industrial scale as well as environmental protection are discussed and illustrated by means of a few spectacular examples. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Innumerable physical, chemical and biological processes take place at the boundary between two phases, while others are initiated at that interface. The change in concentration of a given substance at the interface as compared with the neighbouring phases is referred to as adsorption. Depending on the type of phases in contact, we can consider this process in the following systems: liquid–gas, liquid–liquid, solid–liquid and solid–gas.

The major development of adsorption processes on a large, industrial scale deals mainly with the solid–gas [1–4] and solid–liquid [5,6] interfaces, but in various laboratory separation techniques all types of interfaces are applied [7–11]. The term ‘fluid’ is commonly used to denote gas or liquid in contact with the boundary surface of solids.

A basic concept in adsorption occurring at every interface is the real adsorption system. Let us consider this concept in terms of the solid–gas interface. The real adsorption system can be defined as an equilibrium one including the adsorbent being in contact with the bulk phase and the so-called interfacial layer. This layer consists of two regions: the part of gas residing in the force field of the solid surface and the surface layer of the solid. The term ‘adsorption’ deals with the process in which molecules accumulate in the interfacial layer, but desorption denotes the converse process. Adsorption hysteresis is said to occur when the adsorption and desorption curves deviate from one another. In such a case the isotherm possesses a hysteresis loop, the shape of which varies from one adsorption system to another. Hysteresis loops are mostly with mesoporous solids, where the so-called capillary condensation occurs. The material in the adsorbed state is defined as the ‘adsorbate’, but that in the bulk gas or vapour phase prior to being adsorbed is called the ‘adsorptive’. The penetration by the adsorbate molecules into the bulk solid phase is determined as ‘absorption’. The term ‘sorption’ — together with the terms ‘sorbent’, ‘sorbate’ and ‘sorptive’ — is also used to denote both adsorption and absorption, when both occur simultaneously or cannot be distinguished.

The fundamental concept in adsorption science is that named as the adsorption isotherm. It is the equilibrium relation between the quantity of the adsorbed material and the pressure or concentration in the bulk fluid phase at constant temperature.

Apart from the results of the calorimetric measurements, the adsorption isotherm is the primary source of information on the adsorption process. Its strict meaning

can be derived from the so-called adsorption excess concept which was introduced to surface science by Gibbs more than 100 years ago [12] and forms an important tool for describing adsorption phenomena that occur at various types of interfaces. In terms of the original Gibbs treatment, that is appropriate for fluid–fluid interface, the real interface is assumed to be a geometrical plane called the Gibbs dividing surface (GDS). This surface divides two neighbouring, non-interacting homogeneous bulk phases of a hypothetical reference system. Moreover, these phases are supposed to maintain constant concentration of adsorbed component(s) up to GDS. All the extensive properties of a real adsorption system — including adsorption — are referred to the above hypothetical model. The Gibbs approach has a formal character and requires no models of the structure of the interface layer.

As follows from the above considerations, thermodynamic method of Gibbs surface excess does not take into account the concept of real surface phase, its structure and thickness. The Gibbs dividing surface can be situated arbitrarily within the interfacial layer in such a way that at every point the constituent matter is in an identical thermodynamic condition [13]. There is an infinite number of surfaces satisfying this requirement. However, it is possible to replace the Gibbs equilibrium excesses by operational definitions of the surface excesses which do not depend on the position of GDS [14–16]. These operational quantities can be easily connected with the experimental quantities describing quantitatively the phenomenon of adsorption [17]. Strict operational definitions of the surface excesses were introduced by Wagner [18]. They are very useful to clarify the abstract character of Gibbs definitions. Considering the adsorption at the solid/gas interface, where the adsorption of any component is not too weak and its equilibrium pressure is sufficiently small, the identification between the surface excess amount and the total amount of adsorbed substance can be justified. The same remark holds for adsorption of solutes from dilute solutions on solids. However, it should be remembered that taking into account adsorption from solutions in the full range of their concentrations or adsorption from the gas phase (mono- or multicomponent) under very high pressure, we should take advantage of the surface excess concept whose fundamental validity cannot be disputed.

An alternative convention for the thermodynamic treatment of adsorption phenomena was proposed by Verschaffeldt [19] and Guggenheim [20]. In their formulation an interface is treated as a separate surface phase located between two adjacent bulk phases and which has a finite thickness and volume. This phase can be essentially described thermodynamically in a way analogous to bulk phases [21]. By the use of this approach, the adsorption values and all extensive thermodynamic functions are total, not excess, quantities as in the Gibbs method [22,23].

Irrespective of the convention used for description of the solid/fluid interface, the formalism of the phenomenological [24–28] as well as statistical thermodynamics [29–31] may be applied.

The most advanced theories of adsorption are statistical ones, and they should make it possible to calculate *ab initio* the profile of component concentration at the solid–fluid interface using standard methods of statistical thermodynamics

[32–34]. It should also enable determination of orientation of the adsorbed molecules and calculation of the thermodynamic functions characteristic of interface. The *ab initio* methods require knowledge of the analytical form of the intermolecular interaction potentials in the fluid and at the interface space. Taking into consideration current knowledge about these interactions, it is frequently impossible to use these methods for studying most real adsorption systems. Thus, the *ab initio* method, though very promising, can be used thoroughly only in the studies of adsorption of noble gases and simple molecules on well-defined surfaces [35,36].

Therefore at present and in the near future, approximate theoretical descriptions requiring definite but realistic models of the adsorption process will still be of great interest in the studies of adsorption at the solid/fluid interface. In the generally accepted model of the adsorption system, the real concentration profile is replaced by a step function which ‘divides’ the fluid phase between the surface and bulk phases. These phases are at thermodynamic equilibrium with the thermodynamically inert adsorbent which creates a potential energy field above the surface. The inertness of the solid is believed to be true in the case of physical adsorption, but there are several instances when it can be questioned [18].

A complete statistical description is especially complicated by the heterogeneity of the solid materials which include porous adsorbents, i.e. the majority of industrial adsorbents. Assuming thermodynamic equilibrium between the surface and bulk phases we can derive various adsorption isotherms by utilising the equality of the chemical potentials of a given component in coexisting phases. The analytical forms of these equations depend on the assumed models for the surface and bulk phases. The surface phase may be considered as a monolayer or multilayer, and as localised, mobile or partially mobile. The analytical forms of adsorption isotherms are complex due to structural and energetic heterogeneity of the solid surfaces, which is characteristic of a great number of adsorbents used in practice [13,15,37].

The equilibrium between a bulk phase and the surface layer may be established with regard to neutral or ionic particles. If the adsorption process of one or several ionic species is accompanied by the simultaneous desorption of an equivalent amount of ionic species, this process is considered as an ion exchange.

Adsorption can result either from the universal van der Waals interactions (physical adsorption, physisorption) or it can have the character of a chemical process (chemical adsorption or chemisorption). Contrary to physisorption, chemisorption occurs only as a monolayer [7]. Physical adsorption can be compared to the condensation process of the adsorptive. As a rule, it is a reversible process that occurs at a temperature lower or close to the critical temperature of an adsorbed substance.

Physical adsorption is very effective particularly at a temperature close to the critical temperature of a given gas. Chemisorption occurs usually at temperatures much higher than the critical temperature and — by contrast to physisorption — is a specific process which can only take place on some solid surfaces for a given gas.

Under favourable conditions, both processes can occur simultaneously or alternately. Physical adsorption is accompanied by a decrease in free energy and entropy of the adsorption system and, thereby, this process is exothermic.

Experimental studies concerning the development in the measurements of gas adsorption isotherms on solid adsorbents and the various experimental techniques have been reviewed and summarised in detail (see reviews [38–43] and references therein). With regard to the solid–liquid interface the comprehensive literature on the subject was presented by Kipling [44], Everett [45] and Dąbrowski and Jaroniec [16].

Most of the solid adsorbents of great industrial applications possess a complex porous structure that consists of pores of different sizes and shapes. If the pores are slit shaped we can speak of their ‘width’ but for the pores with a cylindrical shape the term ‘diameter’ is frequently used.

In terms of the experience of adsorption science, total porosity is usually classified into three groups. According to the IUPAC recommendation [46], the micropores are defined as pores of a width not exceeding 2 nm, mesopores are pores of a width between 2 and 50 nm, but macropores represent pores of a width greater than 50 nm. The above classification is widely accepted in the adsorption literature. Nowadays, the expression ‘nanopore’ is used to encompass both micropores and mesopores.

The significance of pores in the adsorption processes largely depends on their sizes. Because sizes of micropores are comparable to those of adsorbate molecules, all atoms or molecules of the adsorbent can interact with the adsorbate species. That is the fundamental difference between adsorption in micropores and larger pores like meso- and macropores. Consequently, the adsorption in micropores is essentially a pore-filling process in which their volume is the main controlling factor [47,48]. Thus, as the essential parameter characterising micropores is their volume usually referred to a unit mass of the solid and characteristics of their sizes. This characteristic is expressed by the so-called micropore-distribution function evaluated mainly from the low-concentration adsorption data [49]. Determination of microporous adsorbent specific surface area from generally accepted adsorption equations is only of a formal character, and it can often be misleading.

In the case of mesopores whose walls are formed by a great number of adsorbent atoms or molecules, the boundary of interphases has a distinct physical meaning. That means that the adsorbent surface area has also a physical meaning. In macropores the action of adsorption forces does not occur throughout their void volume but at a close distance from their walls. Therefore, the mono- and multilayer adsorption takes place successively on the surface of mesopores, and their final fill proceeds according to the mechanism of capillary adsorbate condensation [50]. Therefore, the basic parameters characterising mesopores are: specific surface area, pore volume and pore-size or pore-volume distribution. Mesopores, like macropores, play also an essential role in the transport of adsorbate molecules inside the micropore volume.

The mechanism of adsorption on the surface of macropores does not differ from

that on flat surfaces. The specific surface area of macroporous solids is very small, that is why adsorption on this surface is usually neglected. The capillary adsorbate condensation does not occur in macropores.

As mentioned earlier, a main source of information about adsorption and its mechanism is, besides the calorimetric measurements of adsorption heats [42,51], the adsorption isotherm. The fact that the adsorption isotherm is an integral characteristic of a concrete adsorption system is rather rarely highlighted in the literature. It means that all information derived from an adsorption isotherm deals only with a concrete adsorbent and adsorbate. By means of various adsorbates and the same adsorbent, we can obtain quite different information. It is inappropriate to consider that some of them are correct, but others are incorrect (on condition that the adsorption isotherm is reliably determined). Both kinds of information are truly valid and suitable characteristics that should be chosen according to what is required to be measured. The foregoing remarks are true regarding all real adsorption systems, but they are especially important in the case of porous adsorbents which are mostly industrial ones and contain a great variety of pores of different sizes belonging to those of a mixed structure.

The complete and actual terminology, symbols and definitions dealing with physical adsorption at various interfaces — among them those appropriate for adsorption at the solid/gas and solid/liquid interfaces — were prepared by the International Union of Pure and Applied Chemistry [46,52,53].

2. Historical aspects

The history of adsorption science and technology of adsorbent synthesis as well as the industrial needs that provided the driving force are especially relevant with regard to actual practice. That is because many of the processes now in use, and possibly many future developments, have their origins in earlier discoveries. Moreover, in many cases the theoretical concepts, results and usually terminology dealing with physical adsorption date back several decades. Therefore, the state of the art of physisorption will be preceded by a brief review of the main events of the history of physical adsorption, with some emphasis on theory. We will dwell mainly on physisorption at the solid–gas interface.

Justification for giving priority to this interface stems from the fact that both experimental and theoretical studies of adsorption at the solid–liquid interface preceded those from the gaseous phase. However, several equations of isotherms for adsorption at the solid–liquid interface, particularly equations that refer to adsorption from diluted solutions, are derived from the theoretical description of single gases and their mixtures on solid surfaces.

Comprehensive reviews of physical adsorption at the solid–liquid boundary were the subject of several books and monographs ([13,15,16,24–28,44,54] as well as references therein).

2.1. Pioneering experimental age

Although certain phenomena associated with adsorption were known in ancient times the first quantitative observations were carried out by Scheele [55] in 1773 and Fontana [56] in 1777 who reported some experiments of the uptake of gases by charcoal and clays.

The modern application of adsorption is connected with Lowitz's observation [57,58] who used charcoal for decolorisation of tartaric acid solutions as result of organic impurities uptake. Systematic studies of adsorption that date from the work by de Saussure [59,60] started in 1814. He came to the conclusion that all types of gases are taken up by porous substances (sea-foam, cork, charcoal, asbestos), and this process is accompanied by the evolution of heat. Thus, he discovered the exothermic character of adsorption processes, and he was the first to pay attention to the commonness of adsorption. Moreover, de Saussure observed that gases which undergo condensation readily are taken up to the greatest extent by porous substances.

Of very few papers from the 19th century, there should be mentioned those by Chappuis [61–63], Joulian [64] and Kayser [65,66].

Chappuis measured adsorption of ammonia on charcoal and asbestos at a constant temperature. He also found that sulphur dioxide, carbon dioxide and air are taken up by charcoal depending on the pressure of the gas. He made the first calorimetric measurement of heat evolved during wetting of adsorbents by liquids. This problem was also studied by Pouillet [67], Junck [68], Fitzgerald [69], Lagergren [70], Gaudechon [71] and Dewar [72,73].

The term 'adsorption' was proposed by du Bois-Reymond but introduced into literature by Kayser [65,66]. During the next few years, the terms 'isotherm' and 'isothermal curve' were used to describe the results of adsorption measurements at constant temperature. Kayser also developed some theoretical concepts which became basic for the monomolecular adsorption theory.

McBain [74] introduced the term 'absorption' in 1909, to determine a much slower uptake of hydrogen by carbon than adsorption. He proposed the term 'sorption' for adsorption and absorption. It is not always possible to distinguish between these two phenomena and to define them precisely. In doubtful cases, the term 'sorption' and consequently the terms 'sorbent', 'sorbate' and 'sorpitive' should be used.

Practical application of adsorption processes is based mainly on selective uptake of individual components from their mixtures by other substances. Selective adsorption was discovered by Tswett in 1903 [75]. He took advantage of this phenomenon to separate chlorophyll and other plant pigments by means of silica materials. This separation was possible due to different adsorption affinity of silica gel with regard to various pigments. The technique proposed by Tswett has been called as 'column solid/liquid adsorption chromatography'. This discovery was not only the beginning of a new analytical technique, but also the origin of a new field of surface science. The fact that selective adsorption was found experimentally by Dewar in 1904 [76] is little known.

At present, chromatography is a separate well-developed field of knowledge derived from adsorption [77] and one of the most important analytical methods [78–81]. It is commonly applied for industrial separation of complex mixtures [82–84]. The historical development of chromatography is presented in the book by Ettre and Zlatkis [85] that describes some important landmarks of its theory and practice and the scientists who deserve thanks for developing this technique.

For convenience, the main points dealing with the early experimental age of adsorption are chronicled in Table 1.

2.2. Pioneering theoretical age

Isotherm equations that deal with physical adsorption of gases and vapours, give the most important characteristics of industrial sorbents that include, among others, pore volume, pore size or energy distribution and specific surface area. These very specific curves can be interpreted to obtain information concerning the adsorption mechanism strictly connected with interactions between adsorbent and adsorbate molecules, and they give the opportunity to assess the efficiency of industrial adsorbents applied in separation, purification and other utilitarian processes.

The correct interpretation of experimental adsorption isotherms can be realised in terms of mathematical adsorption equations, i.e. in terms of adsorption isotherms. Such equations are derived in close connection with the assumptions concerning a physical model of the adsorption system. The model assumptions are usually a result of experimental observation. The experimental results allow for the formulation of a hypothesis about the character of the adsorption process. This hypothesis can be tested experimentally. If a hypothesis is not disapproved by repeated experiments, it develops into a theory, i.e. a suitable adsorption equation. Thus, a theory is tested in order to explain the behaviour of the adsorption system investigated. A theory always serves as a guide to new experiments and it is constantly tested. *Adsorption science has been developed by an ongoing interplay between theory and experiment.*

There was no such theory that enabled interpretation of adsorption isotherms before 1914. The Freundlich equation [92] was used but it was not justified theoretically. According to McBain [93], the empirical equation mentioned above was proposed by van Bemmelen in 1888 (see Table 2).

The so-called Freundlich adsorption isotherm was also proposed by Boedecker in 1895 [94] as an empirical equation. This equation is known in literature as the Freundlich's equation, because Freundlich [95] assigned great importance to it and popularised its use.

In 1914–1918, there were proposed two independent descriptions of adsorption phenomena. These descriptions are associated with such names as Langmuir [96] and Eucken [97] as well as Polanyi [98,99].

The Langmuir equation initially derived from kinetic studies was based on the assumption that on the adsorbent surface there is a definite and energetically equivalent number of adsorption sites, at each of which one molecule of a perfect

Table 1
Chronology of the early experimental age of adsorption science

Date	Explorer	Significance
3750 BC	Egyptians and Sumerians	Use of charcoal for reduction of copper, zinc and tin ores for manufacture of bronze.
1550 BC	Egyptians	Application of charcoal for medicinal purposes to adsorb odorous vapors from putrefactive wounds and from intestine.
460 BC	Hippocrates and Pliny	Introduced the use of charcoal to treat a wide range of affections including epilepsy, chlorosis and anthrax
460 BC	Phoenicians	First recorded application of charcoal filters for purification of drinking water.
157 AD	Claudius Galen	Introduced the use of carbons of both vegetable and animal origin to treat a wide range of complaints.
1773 1777	Scheele Fontana	Reported some experiments of the uptake of gases by charcoal and clays derived from various sources [55,56].
1786, 1788	Lowitz	Used charcoal for decolorization of tartaric acid solutions as result of organic impurities uptake [57,58].
1793	Kehl	Discussed helpfulness of charcoal for removal of odours from gangrenous ulcer and applied carbons of animal origin for removal of colours from sugar [86].
1794		Charcoal was used in the sugar industry in England as a decolorization agent of sugar syrups.
1814	De Saussure	Started systematic studies of adsorption of various gases by porous substances as sea-foam, cork, charcoal, and asbestos. He discovered the exothermic character of adsorption processes. [59,60].
1881	Kayser	Introduced terms 'adsorption', 'isotherm' or 'isotherm curve'; he also developed some theoretical concepts that became basic to monomolecular adsorption theory [65,66].
1879, 1883	Chapuis	Made the first calorimetric measurements of heat generation during wetting of various carbon by liquids [61–63].
1901	von Ostreyko	Set the basis for commercial development of activated carbons through processes that involve the incorporation of metallic chlorides with carbonaceous materials before carbonization and the mild oxidation of charred materials with carbon dioxide or steam at increased temperatures [87].

Table 1 (Continued)

Date	Explorer	Significance
1903	Tswett	Discovered the phenomenon of selective adsorption, during separation of chlorophyll and other plant pigments by means of silica materials. He introduced the term: 'column solid–liquid adsorption chromatography'. This discovery was not only the beginning of a new analytical technique, but also the origin of a new field of surface science [75].
1904	Dewar	Found selective adsorption of oxygen from its mixture with nitrogen, during air uptake by charcoal [72,73].
1909	McBain	Proposed the term 'absorption' to determine a much slower uptake of hydrogen by carbon than adsorption. He also proposed the term 'sorption' for both adsorption and absorption [74].
1911		The NORIT factory in Amsterdam was founded, now one of the most advanced international manufactures of active carbons.
1911		A wood distillation plant was built in Hajnówka (East Poland), initially manufacturing active carbons solely from wood materials. World War I introduced the problem of protecting humans respiratory tracts from toxic warfare agents.
1915	Zelinsky	Professor of Moscow University was the first to suggest and apply the use of active carbons as the adsorption medium in gas mask [88].
1941	Martin and Syngé	Introduced to laboratory practice the solid–liquid partition chromatography, both in column and planar form [89].
1956	Barrer and Breck	Invented the method of zeolite synthesis. In this year the North-American Linde Company started production of synthetic zeolites at a commercial scale [90,91].

gas may be adsorbed. The bonding to the adsorption sites can be either chemical or physical, but it must be sufficiently strong to prevent displacement of adsorbed molecules along the surface. Thus, *localised adsorption* was assumed as being distinct from *non-localised adsorption*, where the adsorbed molecules can move along the surface. Because the bulk phase is constituted by a perfect gas, lateral interactions among the adsorbate molecules were neglected. On the energetically homogeneous surface of the adsorbent a monolayer surface phase is thus formed. *Langmuir, for the first time, introduced a clear concept of the monomolecular adsorption on energetically homogeneous surfaces* [96,100].

The statement proposed by Langmuir was applied to chemisorption and with

Table 2
Pioneering theoretical age

Date	Name	Significance
1888	Bemmelen Boedocker Freundlich	The so-called Freundlich empirical equation was firstly proposed by van Bemmelen. It is known in literature as Freundlich equation, because Freundlich assigned great importance to it and popularized its use [94,95].
1911	Zsigmondy	Discovered the phenomenon of capillary condensation [129]. This phenomenon is described by the Kelvin equation for cylindrical pores, with the pore width in the range 2–50 nm [50].
1914	Eucken-Polanyi potential theory of adsorption	The basic concept of this theory includes the adsorption potential and the characteristic adsorption curve, which are independent on the temperature [97–99].
1918	Langmuir	Derived for the first time a clear concept of monolayer adsorption, formed on energetically homogeneous solid surfaces (kinetic studies). The statement proposed by Langmuir applied to chemisorption and with some restrictions, to physisorption [96]. The Langmuir studies of gas adsorption by surfaces led to the formulation of a general treatment of reaction kinetics on surfaces. Langmuir realized that surface catalysis is usually preceded by chemisorption, and he interpreted the kinetics of surface reaction in terms of his monolayer equation.
1932	Langmuir awarded the Nobel Prize	In 1932, Langmuir was awarded the Nobel Prize in chemistry for 'his discoveries and researches in the realm of surface chemistry' [103].
1938	BET	The milestone towards development of adsorption science was the multilayer isotherm equation proposed by Brunauer, Emmett and Teller in 1938 [106]. This theory was preceded by two significant papers by Brunauer and Emmett in 1935 [107] and 1937 [108] who, for the first time, were successful in determining — by means of isotherm adsorption of six different gases — the surface area of an iron synthetic ammonia catalyst. They also introduced the point B method.
1940	BDDT	Brunauer, Deming, Deming and Teller proposed a four-adjustable parameter equation, where the forces of capillary condensation were taken into account [118]. This equation as the complex, was rarely used in literature [50].
1946	Dubinin– Radushkevich	Proposed the theory of the volume filling of micropores (TVFM) [125,126]. This approach is based on the potential theory of adsorption introduced by Eucken and Polanyi [97–99].

some restrictions to physical adsorption. The constant parameters of the Langmuir equation have a strictly defined physical meaning (in contrast to the parameters of the empirical Freundlich equation). Its meaning became particularly clear later whilst deriving this equation by Volmer [101] within the formalism of phenomenological thermodynamics and deriving this equation by Fowler within the statistical thermodynamics [102] as well. The Langmuir equation describes relatively well physical (or chemical) adsorption on solid surfaces with one type of adsorption active centre.

Langmuir tried to extend his theoretical approach to account for heterogeneity of solid adsorbent and the multilayer character of adsorption. He noticed that one of the fundamental assumptions of his theory which refers to the homogeneity of the adsorbent surface is not justified in many cases. Surfaces of most solids are energetically heterogeneous because the adsorption sites are distributed over energetically different levels [100].

It is noteworthy that the Langmuir studies of gas adsorption led to the formulation of a general treatment of the kinetics of reactions at surfaces. Langmuir stated that the surface catalysis is usually preceded by chemisorption, and he interpreted the kinetics of surface reactions in terms of his monolayer equation. He also showed how the adsorption isotherm could be applied to interpret the kinetics of a variety of surface reactions. These fundamental investigations in the field of surface catalysis provided the background for detailed and extended studies that are carried out today as a result of the industrial importance of catalysis. In 1932, Langmuir was awarded the Nobel Prize in chemistry for 'his discoveries and researches in the realm of surface chemistry' [103].

Later some attempts were made to generalise the Langmuir equation by taking into account lateral interactions among adsorbed molecules, their mobility and the energetic surface heterogeneity of the solids. The Langmuir equation itself should be considered, however, as a useful equation that corresponds to the so-called ideal localised monolayer. The ideal localised monolayer model, despite its obvious imperfections, occupies a central position in surface and adsorption science. It allowed for a start of comprehensive theoretical studies, the aim of which was and still is a search for more and more perfect and real descriptions of experimental adsorption systems [104,105].

Another milestone towards development of the adsorption science was the multilayer isotherm equation proposed by Brunauer et al. in 1938 [106]. The multilayer adsorption theory was preceded by two significant papers by Brunauer and Emmett which appeared in 1935 [107] and 1937 [108].

Brunauer and Emmett proposed also for the first time to determine the monolayer adsorption amount from the so-called point B of the experimental isotherm [107,108].

At first the BET equation was derived from the kinetic considerations analogous to those proposed by Langmuir whilst deriving the monomolecular adsorption isotherm. The first statistical thermodynamic derivation was carried out by Cassie [109]. Lately, a slightly modified derivation has been proposed by Hill [110–112] and Fowler and Guggenheim [113].

The principal assumption of the BET theory is that the Langmuir equation applies to every adsorption layer. Like the Langmuir theory, the first adsorption layer is formed on an array of surface sites of uniform energy. The major simplifying assumptions deal with the foundation, that — beginning from the second adsorbed layer — the condensation heat is equal to the evaporation heat of gas and that the ratio between the rate constant of uptake from one layer and the condensation of a lower situated layer for all the layers starting from the second one, is the same. Later, these assumptions were extensively discussed in literature [114–117]. *The BET isotherm represents a generalisation of the Langmuir isotherm, to some extent.*

The BET adsorption isotherm was originated for a definite model of adsorption layer [106], and next, it was extended to the finite, n -number of layers [118,119].

An alternative well-known approach to multilayer adsorption was proposed by Frenkel, Halsey and Hill, usually called the FHH slab theory [120]. Later, several modifications of the BET equation were proposed [121–123], but those did not find wide acceptance for studying gas and vapour adsorption processes [50].

In 1940, Brunauer et al. [118] extended the BET theory by introducing an additional contribution to the energy of adsorption that results from the forces of capillary condensation. The so-called BDDT equation, contrarily to the BET isotherm, can be applied over a wider range of relative pressures. This equation is rather complex, and it contains four adjustable parameters that cannot be assessed independently [121].

Another important contribution by Brunauer et al. [118] deals with the identification of five principal types of adsorption isotherms for gases and vapours. This identification is known as the BDDT classification, and it is recommended as the basis for a more complete classification of adsorption isotherms introduced by IUPAC [52].

The BET theory, despite many restrictions, was the first attempt to create a universal theory of physical adsorption [124]. It describes the entire course of the isotherm including the areas of monomolecular adsorption, polymolecular adsorption and capillary condensation. Unfortunately, the last region is described in an unsatisfactory way, particularly, if the solid is of a heterogeneous porous structure that comprises pores of various capillary widths. This theory cannot be applied to adsorption at temperatures higher than the critical temperature because it is not possible to assume equality of heats of adsorption and condensation as well as stability of the adsorption coefficient ratio with regard to individual adsorption layers.

Nevertheless, the so-called BET low-temperature nitrogen method is still widely applied as the standard procedure for determining the specific surface area of fine powders and porous materials [122].

The Langmuir and BET theories, originating from one common assumption, assume the existence of an interface geometrical surface on which mono- or multilayer adsorption takes place. *The basic geometrical parameter applied to flat macroscopic adsorbents is their surface area.*

However, Langmuir [100] supposed that adsorption on adsorbents that possess narrow pores proportional to the sizes of adsorbed molecules must proceed according to a different mechanism. With any character of adsorption interactions causing physical adsorption in the entire area of micropores, a strong adsorption field appears in them. A limited space of micropores causes the next molecules adsorbing in micropores to not form adsorption layers, but they fill up micropores in respect of volume according to the mechanism of micropore filling. Therefore *a basic geometrical parameter characterising microporous adsorbents is the volume of micropores but not their 'surface'*.

Adsorption theory of the volume filling of micropores (TVFM theory) has been proposed by Dubinin and Radushkievich [125], but this approach has originated from the potential theory of adsorption introduced by Eucken [97] and Polanyi [98,99]. However, Dubinin [126] — in contrast to Polanyi who defined the differential molar work of adsorption A as the adsorption potential — introduced the adsorption potential as the negative work performed by the sorption system which is $A = -\Delta G$, giving thus opportunity to open gate to thermodynamics.

According to their concept, the adsorbed layer has a multilayer character, therefore it is not two-dimensional as follows from the Langmuir theory, but it possesses a definite volume and applies to the van der Waals equation. The assumptions underlying the so-called potential theory of adsorption commonly named the Polanyi theory originates from the earlier work by de Saussure [59,60]. According to this assumption the adsorbed layer is considered as the 'thick', multilayer film of decreasing density and increasing distance from the solid surface. The basic concept of the Polanyi theory includes the adsorption potential and the characteristic adsorption curve. This characteristic curve presents a simple relationship between the adsorption potential and the distance from the solid surface. This relationship was named as the characteristic adsorption equation. The aforementioned distance may be expressed in terms of volume units of the adsorbed phase. Polanyi assumed [98,99] that the adsorption potential is independent of temperature over a wide range of the latter. It means that the characteristic curve of adsorption is temperature independent, too. Such a statement follows from the fact, that the van der Waals forces are also independent of temperature. However, for polar adsorbates this does not always hold true.

Having calculated the curve characteristic for a given temperature it is possible to determine adsorption isotherms at other temperatures. The Polanyi potential theory does not give a definite equation of adsorption isotherm which, to some extent, replaces the characteristic adsorption equation [127,128].

The Polanyi theory that assumes the description of a three-dimensional layer adsorbed by the van der Waals equation, implies not only that the adsorbate concentration increase at a suitably low temperature, but also its condensation into a liquid which takes place on the adsorbent flat surface. In contrast to condensation, that can proceed only on the flat surface of a solid, the capillary condensation which takes place if the adsorbent has a porous structure should be distinguished.

The capillary condensation phenomenon was discovered by Zsigmondy [129] who investigated the uptake of water vapour by silica materials. Zsigmondy proved that

condensation of physisorbed vapours could occur in narrow pores below the standard saturated vapour pressure. The main condition for the existence of capillary condensation is the presence of a liquid meniscus in the adsorbent capillaries. As known, the decrease of saturated vapour pressure takes place over concave meniscus. For cylindrical pores, with the pore width in the range 2–50 nm, i.e. for mesopores, this phenomenon is relatively well described by the Kelvin equation [50]. This equation is still widely used for pore size analysis, but its main limitations remain unresolved. Capillary condensation is always preceded by mono- and/or multilayer adsorption on the pore walls. It means that this phenomenon plays an important but secondary role in comparison with physical adsorption of gases by porous solids. Consequently, the true pore width can be assessed if the adsorbed layer thickness is known.

Zsigmondy, as the first, paid attention to adsorption on the capillary inner walls, which is primarily referred to as capillary condensation [129]. This unusually correct observation corresponds to modern views regarding processes of gases and vapours uptake by porous (i.e. industrial) adsorbents. Such a process as a rule includes mono- and multilayer adsorption followed by capillary condensation in the final stage of uptake. A quantitative part of capillary condensation in the uptake of a given vapour varies for different adsorbents depending on their porous structure. This process is dominant for adsorbents where mesopores comprise a larger part of porosity [130].

A very important characteristic of capillary condensation is the so-called hysteresis loop that occurs on many experimental adsorption isotherms. According to Foster [131] and Cohan [132], the adsorption branch of a hysteresis loop is caused by polymolecular adsorption and capillary condensation but the desorption branch appears only due to the condensation phenomenon.

De Boer [133] classified the capillary hysteresis loops according to their shapes, relating the latter to the occurrence of pores of given types. He distinguished five types of hysteresis loops with one vertical or steep branch. Due to the non-homogeneous porous structure of most adsorbents, the experimental hysteresis loops of adsorption–desorption isotherms are a combination of two or more types described by de Boer.

An important contribution to explanation of the hysteresis feature was made by Everett and coworkers [134–138].

Up to this day, various attempts have been made to assess the mesopore size distribution function by means of the capillary condensation part of adsorption isotherms. Following the IUPAC recommendation [130], these procedures should be applied carefully in order to obtain reliable results.

At present the Polanyi theory has a rather historical meaning. However, the theory of volume filling micropores (TVFM) also called the Dubinin–Radushkevich theory [47,125] which is generally accepted, though always improved, originates from the Polanyi theory. TVFM has significant importance for the characteristic of most industrial adsorbents which have a well-developed porous structure, e.g. [139–141].

The DR equation, unlike the Langmuir and BET equations, is not based on a defined model process to describe physisorption of gases. It is rather based on considerations of adsorption energies. The excellent reviews of this equation, its applicability and limitations were presented in quite recent monographs [41,142].

The Dubinin–Radushkevich equation with its numerous modifications is very important for the adsorption methods of characteristics of most industrial adsorbents which have a complex and well-developed porous structure including pores of different shapes and widths, but micropores play the most significant role in the structure.

As is known, adsorption can be considered as a physical or chemical process. The forces responsible for any type of adsorption are named adsorption forces. The theory of adsorption forces was developed by London [143,144], de Boer and Custers [145], Lenel [146] and de Boer [147,148]. The studies by Lennard–Jones [149], who proposed the so-called Lennard–Jones attraction–repulsion (6–12) potentials were of significant importance. Development of mechanics and quantum chemistry (e.g. [150]) had a great influence on understanding the character of interactions both in physical and chemical adsorption as well. Excellent reviews on development of adsorption forces have been presented in several papers and monographs [121,151–153].

Discussing and comparing the basic adsorption theories presented so far, it is difficult to say which one is fundamentally correct. The Polanyi thermodynamic theory neither determines a definite adsorption isotherm equation nor gives a detailed mechanism of the process. Development of this theory for description of adsorption on microporous solids leads to the analytical DR equation but its character remains semi-empirical.

The Langmuir equation and the method of solid surface area determination based on it can be applied to systems in which the adsorption process is not complicated by formation of a multilayer or by adsorption in micropores and capillary condensation.

The BET equation that reduces to the Langmuir equation in the area of low relative pressures describes adsorption relatively well in the area of relative pressures of 0.05–0.35. It means that the agreement of experimental data with this equation is included in rather a small area. The more typical deviations that result from application of the BET equation, consist of the fact that it predicts too small adsorption values at low pressures and too large at high pressures. The BET equation allows the correct calculation of the specific surface area of macroporous adsorbents and transiently porous ones lacking a great number of micropores. The presence of micropores volume filling by adsorbate molecules in the adsorbent leads to incorrect results, though in a definite range of relative pressures, the experimental data can correspond to a linear form of the BET equation.

Thus, the BET theory can be applied only in the area of medium values of relative pressures, i.e. after formation of a monolayer. Moreover, in the area of relative pressures under consideration, capillary condensation does not generally appear. In some cases, the BET equation gives satisfactory results in the range of relative pressures up to 0.5 [50]. In the capillary condensation area, the BET theory

should be used cautiously, in particular, if the adsorbent is characterised by a large spectrum of capillary sizes. In this area, the Kelvin equation is usually applied. Finally, the BET theory cannot be used to describe adsorption on microporous adsorbents where the DR isotherm is an expression considered to be correct.

The least of all we demand from any theory is that it describes the free energy change accurately. This is related to differing enthalpy and entropy effects at varying degrees of coverage of the adsorbent surface. The enthalpy and entropy contributions that arise from the BET and also the Langmuir theory agree at best semiquantitatively with experiment [121]. The calculated enthalpy values are too small and the entropy values too high. Therefore there are several doubts as to the applicability of the physical picture given by both BET and Langmuir theories. The above remarks demonstrate that the extension of the theory of gas or vapour adsorption to cover the entire range of pressures has not been successful, in the first period of adsorption science. Thus, *the next step in the studies of adsorption will be continued to lead to even better results, providing a more accurate description of the true mechanism of adsorption from the gaseous phase.*

At this point, it should be stressed that a general theory of adsorption that would include all factors affecting a given process, can lead to such a complicated equation of isotherm that it could describe correctly each experimental isotherm independently of this shape. Such an equation would be totally useless because none of the constants that occur in it could be determined experimentally. *It often happens that simplicity of a given theory can be its greatest advantage at the same time.*

Finally, it should be stated that only the most important concept and equations of adsorption isotherms were discussed. Isotherms that include lateral interactions between molecules in the surface monolayer as well as equations that deal with mobile and mobile-localised adsorption were omitted. These equations can be derived in a simple way by assuming that molecules in the surface phase form the surface film whose behaviour is described by the so-called surface equation of state. This equation is a two-dimensional analogue of the corresponding three-dimensional equation of state, and it relates the surface pressure (spreading pressure) of the film to the adsorption. This adsorption can be expressed by the Gibbs adsorption isotherm [12]. Consequently, it is possible to interconvert the adsorption isotherm and a surface equation of state by means of the Gibbs adsorption equation. Assuming various pictures for the two-dimensional adsorbed gas, the various adsorption isotherms were developed. Among them, therefore, the Henry law for ideal non-localised monolayer [50], the Langmuir equation for ideal localised monolayer [121], the Volmer [121] and Hill–de Boer [148,154] equations for the non-ideal and non-localised monolayers, and the Fowler–Guggenheim [155] equation for the non-ideal, but localised monolayers. On the other hand, the above equations can be derived by means of the formalism of statistical thermodynamics [154,155]. The two-dimensional equations of state were very useful for investigating phase transitions in the adsorbed layers [7,121].

The above considerations did not include basic concepts of adsorption kinetics and dynamics on porous adsorbents and in the heterogeneous catalysis process.

The fundamental field of science dealing with adsorption, i.e. adsorption thermodynamics was also omitted. Even a brief discussion of these problems goes beyond the limits of this chapter. For more information, cf. [4,7,8,20,25,37,49,88,95,144,147,154–161] and references therein.

On the other hand, the equations and definitions presented above are the most fundamental ones for adsorption science although more than 50 years have elapsed since their publication. As will be seen later, a large part of modern adsorption theory is derived directly from those equations. Moreover, these equations play a fundamental role in the studies of structure of most industrial adsorbents and solid catalysts.

Catalysis, particularly heterogeneous catalysis, is closely connected with adsorption, though in contrast to chromatography, it was a separate field of knowledge during the initial, empirical period and its development. At present, it is known that the action of solid catalysts is inseparably connected with their adsorption properties regarding reactants and other requirements concerning industrial adsorbents and catalysts. For these reasons it is advisable to discuss briefly this very important branch of surface science.

3. Catalysis and its relationship with adsorption

Catalysis plays a most outstanding role in modern industry, environmental protection and our everyday life. Moreover, its importance in sustainable development is beyond discussion [162–164].

Approximately, it accounts for as much as 90% of chemicals and materials manufactured throughout the world. *Catalysis, as a vital process, is the technology of the 21st century.*

To give a comprehensive description of practical applications in which catalysis is an essential feature, it requires a book or books itself (see references [7,164–168] and references therein). Besides, this section is not an attempt to review the applications of catalytic technology in the field of every modern life. Rather, *the aim is to highlight the relation between catalysis and adsorption, which should be considered as the most important domain of surface science.*

Catalysis is not a new phenomenon, but its wilful utilisation by humans has really begun in this century. Enzymatic catalysis is necessary for all living matter. Most essential of all catalytic processes is photosynthesis which underlies most of the simplest and earliest evolved life forms.

One of the first catalytic processes was probably fermentation of fruits in order to obtain alcoholic beverages [165]. Here, the natural catalysts are yeast-contained enzymes which convert sugar into alcohol. In fact, ancient Sumerians described the beer preparation on clay plates many millenia ago. Systematic studies of the phenomenon under consideration began at the beginning of the 19th century. In 1815, Davy performed experiments that dealt with catalytic combustion on platinum gauzes. The term ‘catalysis’, however, was introduced by Berzelius in 1836 [169].

The term catalyst denotes a body or a material which accelerates a chemical equation but does not appear either in the reactants or products of a chemical equation of this reaction. It enhances the rate of the reaction, and is finally regenerated at its end. Usually, catalysts are classified as both homogeneous and heterogeneous catalysts. Homogeneous catalysts occur in the same phase as the reactants, but heterogeneous catalysts are in a different phase. Heterogeneous catalysis includes heterogeneous catalysts that are typically solids. Besides, the important subdisciplines of the process under consideration are biological, enzymatic and photo-catalysis [165].

The prerequisite to heterogeneous catalysis to occur is adsorption (usually chemical one) of molecules of the reacting substances on the inner or outer surface of the adsorbent or of the catalyst; then molecular dissociation of at least one or two reacting components, usually preceded by surface diffusion [163].

The next step is a surface reaction which is often rate-determining in a catalytic reaction. Then desorption of the product occurs because the surface bond is broken, and the final product enters the bulk phase, diffusing through the catalyst pores. This very simple picture highlights the basic idea of heterogeneous catalysis. *This scheme also points out clearly that development of adsorption science — including theory, practice and achievements of preparation and production of new solid sorbents — is a main factor conditioning development of heterogeneous catalysis.* Nowadays, a broad range of advanced catalysts is used to facilitate numerous chemical reactions. Among others, the role of catalysts is displayed by [170]: metals or metal complexes grafted individual sites on high area micro- or mesoporous solid supports, enzymes, antibodies, ribozymes, membranes — ceramic or biological — and nanoparticles.

Moreover, there is a great variety of adsorbents which, depending on the chemical structure of their internal or external surfaces, act as solid catalysts or their supports. The basic function of catalyst supports is to keep the catalytically active phase in a highly dispersed state. For this reason, catalyst supports are usually porous adsorbents characterised by a well-developed inner structure and a large specific surface area. The latter, however, is not always desirable.

Catalysis, contrary to chromatography, is not derived directly from the science of adsorption. However, it cannot be considered apart from adsorption, particularly from adsorption at solid–gas and solid–liquid interfaces. As is generally known, most adsorbents act as catalysts or their supports. Therefore, methods of preparation and characterisation of adsorbents and catalysts are very similar or identical. Physical structure of catalysts is investigated by means of both adsorption methods and various instrumental techniques derived for estimating their porosity and surface area [165].

The most fundamental characteristic of any industrial catalyst is its chemical composition. Other factors, such as surface area, distribution of pore volumes, pore sizes, stability and mechanical properties, are also very important. Such catalysts as metals or oxides of various types (pure or mixed) are not necessarily thermally stable in their high surface area modification in which they have to be applied. So,

they are prepared as small particles bound to the support material, usually oxides, such as alumina and silica gels.

Activated carbons, due to their porosity and chemical surface composition, both of which may be controlled appropriately, are also recommended as suitable catalyst supports [167]. On the other hand, both silica and alumina species as well as natural amorphous aluminosilicates and zeolites are widely used as heterogeneous catalysts. These adsorbents that have acid or/and base sites are called as solid acid–base catalysts [171].

In the 1960s, an important group of catalysts was developed utilising synthetic zeolites which have open, well-controlled framework structures that create interconnected cavities [172].

Especially, microporous aluminium phosphates and metal substituted aluminium phosphates can be routinely manufactured [173]. Synthetic microporous zeolites are nowadays of central importance industrially, as they are the powerful acid–base catalysts. These microporous materials have usually pore diameters in the range from 0.3 to 1.8 nm. By means of ion-exchange of alkali metals for proton components acid catalysts whose acidity can be many times higher than that of sulfonic acid, can be obtained [170]. An important feature of zeolite catalysts deals with their three-dimensional framework of channels and cavities, to give possibility for selection of reactants and products due to the dissimilarity of their molecular sizes and shapes. Other important perspectives of huge practical importance are connected with the so-called mesoporous catalysts, exhibiting unique properties and prepared by a revolutionary synthesis method. These so-called MCM-41 mesoporous (Mobil Crystalline Material, number 41) first reported in 1992 [174], offer new possibilities in a generation of shape-selective catalysts and as supports for the metal-based catalytic sites. Their typical pore dimensions of the channels are 2–10 nm, with the internal surface areas exceeding 1000 m²/g. The mesoporous MCM materials may be easily modified by incorporating various heteroatoms into their framework [175]. A comprehensive review can be found in [176].

A new class of solid acid–base catalysts is developed from mineral clays [171]. These materials have a two-dimensional layer lattice in which oxyanions are exchanged by hydrated cations. These intercalated cations with acid properties form so-called pillared clays [177] that have structural cavities — whose sizes can be controlled — similarly to those in zeolites. Both three- and two-dimensional solid acid catalysts are very useful for selecting reactants and products of catalytic processes, among them some isomers of profound petrochemical significance [178]. The role of special catalysts is played by well-known Keggin heteropoly acids. The catalysts of a regular structure (zeolites, clays and heteropoly acids) as well as their synthesis, mechanisms of reactions in them, can be designed and investigated by means of the Monte Carlo, molecular dynamics and quantum mechanics methods [179–183].

Rationally designed, both microporous and mesoporous inorganic catalysts are already the facts for many industrial and environmentally compatible technologies [165].

From the above remarks about catalysis the following conclusions can be drawn:

1. adsorption and catalysis are closely related to each other;
2. the action of solid catalysts results from their capability to adsorb reacting substances;
3. the same porous solids can be used as adsorbents, catalyst supports and catalysts;
4. the chemical character and size of solid surface areas, their porous structure, mechanical properties and thermal stability play an essential role in adsorption and catalysis; and
5. the development of theoretical studies on adsorption, design and manufacture of new adsorbents affects heterogeneous catalysis development.

4. Current state of physical adsorption

The first period of development of adsorption theory and adsorption experiments was based mainly on the Langmuir and BET equations, capillary condensation theory, Polanyi potential theory and the DR equation related to the latter. This first period of adsorption development, named as the ‘pioneering age’ of adsorption science [184], ended on the turn of the 1940s and 1950s. At that time the above theories and equations of adsorption isotherms were extensively verified experimentally and improved theoretically. The improvements included mainly interactions between adsorbed molecules, localised and mobile-localised adsorption as well as studies of phase transitions in the adsorbed layers (e.g. [121] and references therein).

In spite of many improvements of the Langmuir and BET equations, distinct deviations from experiment were observed particularly in the range of small and high relative pressures. The attempts to fit the experimental isotherms by theoretical equations showed negative deviations from the experimental points at low adsorbate pressure and positive deviations at higher bulk phase pressure. The most dramatic deviations were observed with regard to the measurements of the enthalpy changes upon adsorption. On the other hand, the theoretically predicted isosteric heats of adsorption should be an increasing function of the surface coverage, but almost all the reported experimental heats showed an opposite trend. The above mentioned disagreements between theory and experiment point out that there must exist an additional physical factor that influences adsorption processes, which can be compared with the effect resulting from interactions in the adsorbed layer; and this factor had not been taken into account by the existing theories. This missing factor deals with the energetic heterogeneity of the most real solid adsorbents.

4.1. Adsorption on heterogeneous solids

4.1.1. Adsorption of single gases

A new period of adsorption development is connected mainly with intensive

theoretical and experimental studies of physical adsorption of gases, their mixtures as well as liquid solutions on heterogeneous solid surfaces.

The concept of surface heterogeneity is in agreement with general concepts regarding the solid state theory. Real solids have a polycrystalline and amorphous structure. Fine crystals of various sizes create grains of different forms and sizes. Beside cracks, fissures and other defects on the solid surface whose existence can be detected by means of various observation methods, heterogeneity is caused by disturbances in the crystal lattice corresponding to the difference between the real structure and the ideal crystal lattice. Beside dislocation of surface atoms, another type of disturbance can result, among others, from lattice defects of the Frenkel or Schottky type. Finally, heterogeneity can be caused by impurities whose presence can affect significantly the surface properties of adsorbents, particularly of catalysts. The surface heterogeneity plays an important role in the adsorption on crystalline and non-crystalline, nonporous, mesoporous and macroporous solids. However, the main source of heterogeneity for microporous solids is their complex porous structure which contains micropores of different dimension and shape. The distribution of micropores makes the main source of the heterogeneity of a microporous structure. On the other hand, the adsorption potential distribution energy and micropore-size distributions evaluated from the low pressure branch of adsorption isotherms are the main characteristics of structural and energetic heterogeneities of microporous and nanoporous materials.

Defects and disturbances in the solid structure and, thus, in its surface cause that the interaction between adsorbing molecules and this surface varies in different points. It means that the adsorption energy value depends on which area of the surface adsorption it takes place. In a given area, the adsorption energy value is constant and elementary theories of adsorption are applicable. Thus, the process that occurs on the whole heterogeneous surface can be considered, in a first approximation, as a result of summing up independent processes that take place on individual areas of the surface or active centres.

Based on this assumption, Langmuir [96] was the first to observe that for adsorption from the gas phase on polycrystal surfaces, his equation with suitably chosen constants could be applied to describe adsorption on certain kinds of sites and that the experimental adsorption data can be approximated by a sum of Langmuir equations, each multiplied by the fraction of a given kind of site on the solid surface. If the number of areas with different values of energy is very large, energy changes continuously and summation is replaced by integration. The concept of integral adsorption equation was first introduced by Zeldowitsch [185] in 1934. This author derived the overall adsorption isotherm being the Freundlich equation. However, the first wilful application of the integral adsorption equation is associated with Schuchowitzky [186] and Roginsky et al. [187–190]. Roginsky assumed the so-called continuous energy distribution function and proposed the use of the Stieltjes transform method for solving the adsorption integral equation. The next important step in terms of this approach was proposed by Roginsky and co-workers [189] and further by Todes and Boundareva [191], who introduced the concept of the condensation approximation (CA). The CA concept deals with the

assumption that adsorption process proceeds gradually when adsorbate pressure increases on adsorption sites with decreasing adsorption energies. At a given temperature and pressure, the adsorption sites that have the so-called critical adsorption energy are completely covered, but others are totally empty. Thus, the critical adsorption energy corresponds to some critical temperature T_c and critical pressure p_c .

The integral adsorption equation gives the following possibilities: (1) analytical forms of the overall isotherm for various analytical forms of the adsorption energy distribution function assumed a priori; (2) analytical forms of the energy distribution function for the overall adsorption isotherms assumed a priori; and (3) numerical values of the adsorption energy distribution for an overall experimental adsorption data set. Consequently, the integral adsorption equation gives an opportunity to determine the mutual inter-dependence between the shape of the overall adsorption isotherm and the energy distribution function. *This distribution offers a quantitative characterisation of global adsorbent heterogeneity but provides no information with regard to distribution topography of the adsorption sites.* At the end of the 1940s and at the beginning of the 1950s, work on physical adsorption of gases on energetically heterogeneous solid surfaces became an object of interest to many American scientists [192–198]. Among others Sips [193], using the Stieltjes transform method, derived an overall adsorption isotherm in the form of the Langmuir–Freundlich equation and the so-called generalised Freundlich equation. In the same way, the Temkin [199] and Tóth [200] empirical equations were justified.

Initially, the first two possibilities of integral adsorption equation were intensively explored by investigators who used almost exclusively the Langmuir adsorption isotherm [201–210]. Then, the type of the topography of adsorption sites is of free choice. The mathematical forms of the overall adsorption isotherms depend only on the shape of the energy distribution functions, that characterise the global heterogeneity of the adsorbent surface. In terms of this approach, the Freundlich and Dubinin–Radushkevich equations were derived as the overall adsorption isotherms for adsorption on heterogeneous solid surfaces. As mentioned earlier, the DR equation is a fundamental equation for adsorption from the gas phase by microporous solids. However, Hobson [211] realised its great applicability for a description of gas adsorption on real flat surfaces that comprise those of non-porous, porous as well as mesoporous materials. Hobson [212] was also the first who used the condensation approximation method to find the analytical form of energy distribution related to the DR equation. The most advanced studies with regard of theoretical foundation DR equation applicability, were made by Cerofolini [213,214]. Cerofolini [215,216] launched a well-documented hypothesis that the so-called DR behaviour of numerous experimental systems is related to the rules governing the formation of real surfaces. The same conclusions were true of the Freundlich equation.

The further development of extensive research in the 1970s and 1980s deals with local isotherm equations that take into account the interactions between the adsorbed molecules [217]. In such a case, the model of heterogeneous solids that

assumes a definite distribution of adsorption sites on the surface must be exactly defined ([218], and references therein).

Two main models of heterogeneous surface are frequently used in adsorption, viz. patchwise and random models. The patchwise model was suggested by Langmuir [96] and popularised by Ross and Olivier [217]. In this model the adsorption sites of equal adsorption energies are assumed to be grouped together into patches. These patches are so large that the interactions between two molecules adsorbed onto different patches can be neglected. The random model of adsorbent surfaces, in which the adsorption sites of equal adsorption energies are assumed to be distributed fully at random over a heterogeneous surface was introduced by Hill [195]. This last model seems to be more realistic for a majority of real adsorbents, especially towards the adsorption from the gas phase [13]. Jaroniec and co-workers considered also models with medial and regular distributions of adsorption sites on the surface [219,220]. In recent years, new types of heterogeneous surfaces have emerged that cannot be classified in either of the basic models (patchwise or random) discussed above. These models, including also fractal surfaces, were discussed by Cerofolini and Re [221]. Later, an alternative concept of adsorbent heterogeneity was proposed for adsorption on microporous solids with micropores of different dimensions and shapes [222,223]. Such micropores are a source of structural heterogeneity, which may be described by the micropore-size distribution function. On the other hand, surfaces of meso- and macropores generate the surface heterogeneity. The total adsorbent heterogeneity is a simple sum of both structural and surface heterogeneities and is usually characterised by the adsorption energy distribution function. This distribution function may be evaluated on the basis of the overall experimental adsorption isotherm. However, homogeneous microporous adsorbents have micropores of identical shapes and dimensions. Consequently, a homogeneous microporous adsorbent is energetically heterogeneous. Thus, the concept of energetic heterogeneity is more universal and may be applied to describe the heterogeneity effects in adsorption on non-porous and porous solids [219].

Another important progress in physical adsorption deals with description of multilayer adsorption of gases on heterogeneous surfaces. In this case the most considerations are based on the following assumptions: (1) energetic heterogeneity of the adsorbent surface is restricted to the first layer only; and (2) lateral interactions in each adlayer are neglected. Assumption (2) means that the kind of topography of adsorption sites is of no significance. As local equations there were used the classical BET equation [224], n -layer BET equation [224–226], and the so-called Jovanovic isotherm [227]. Cerofolini [221,228] initiated a new set of papers on multilayer adsorption on heterogeneous surfaces. In contrast to numerous analytical solutions of the integral equation for multilayer adsorption, numerical studies were scanty. Typical papers on this subject were published by Jaroniec and Rudziński [224] and Hsu et al. [229]. Both the n -layer and infinite layer models of the surface phase were taken into account. The results published in the above papers were successfully compared with experimental data.

So far papers were reported which retained the Langmuir assumption that each adsorbed molecule occupies one site on the surface. While this assumption may be justified for small molecules, it is unlikely to be realistic for large ones, and often more industrially important molecules such as the *n*-alkanes.

Contemporary theory on the multi-site occupancy adsorption on heterogeneous solid surfaces is fairly meagre. The reason is that such description involves a new degree of complexity, and only a few papers have been published on this subject [230,231]. Rudziński and co-workers [232–235] accepted the Everett equation for multisite occupancy adsorption from liquid mixtures [236] on solid surfaces as a starting expression to describe adsorption on heterogeneous surfaces with random and patchwise topography. A short review on the subject is presented in reference [237].

In the 1970s and 1980s a dozen of numerical methods were proposed in order to find the distribution energy functions of adsorption on the basis of tabulated data of experimental adsorption isotherms.

The following list includes the most popular and useful of them:

1. discretisation methods, in which the solution of the integral equation is reduced to the inversion of a square matrix [238,239];
2. optimisation methods based on the choice of an analytical form for the distribution function that contain some parameters to be determined subsequently by a best fit of the calculated overall isotherm to the experimental data [240–242];
3. regularisation methods, in which the ill-posed problem is replaced by a stable minimisation problem in various ways [243–246];
4. iterative methods that use various iterative algorithms in order to improve an initial guess for the distribution function [247–249];
5. expansion methods that are based on the expansion of all functions to appear in integral equations in series of a complete orthonormal set [250–252]; and
6. integral transform methods that are based on analytical methods in which the experimental isotherm is approximated by a suitable interpolating expression and the analytical inversion formula is expressed in an easily computable form [221].

As follows from the hitherto existing considerations, the adsorption integral equation can be solved considering the distribution function in an analytical and numerical way. Approximate methods comprise another set of methods used for solution of this equation. These methods are based on the above mentioned condensation approximation (CA) approach. This method leads to simple analytical expressions for the distribution functions in terms of the derivative of the global isotherm. The CA method was improved by Hobson [253] and Cerofolini [254] who proposed the so-called asymptotically correct approximation (ACA). It is based on the replacement of the true local isotherm by an approximate kernel of the integral equation which shows correct asymptotic behaviour at both low and high pressures. A comparison between the CA and ACA methods was presented in paper [216].

Another approximation method, that originates from the CA approach was proposed by Rudziński and co-workers [255–257]. This so-called third-order approximation was developed without assuming a local isotherm approximation. Rudziński found that his method gives results remarkably better than those obtained by the CA and ACA approaches. Another approximation method for solving the adsorption integral equation with regard to the energy distribution function was proposed by Nederlof and co-workers [258]. The main advantage of the above approximated method deals with [221]: (1) the stability of the obtained solutions; (2) the simplicity of the expressions for the distribution function; and (3) the local character of the solutions, i.e. the fact that the calculation of a distribution function in one point does not need the knowledge of the entire isotherm.

Another important method for estimating surface heterogeneity is based on calorimetric measurements of energetic effects of adsorption which are more sensitive to the nature of a particular adsorption system than adsorption isotherms [257,259–263]. This method is promising for characterisation of adsorbent heterogeneity, but it needs accurate calorimetric data for a given adsorption system [264].

Recently, thermal desorption [265,266] and adsorption kinetics measurements on heterogeneous surfaces [267–269] were proposed for an evaluation of energy distribution functions. These methods have been tested extensively during the last few years.

In 1974, Steele published his famous book *The Interaction of Gases with Solid Surfaces* [30] which is considered as important guidelines for scientists to investigate the nature of solid–gas interactions in terms of the so-called virial formalism. This trend in theoretical studies of physical adsorption is very fruitful, and numerous papers have been published on this subject (e.g. [270] and references therein).

The numerical values of the second, third and fourth two-dimensional virial coefficients give qualitative information on the interactions between adsorbed molecules and adsorption sites as well as on the interactions among suitable numbers of admolecules. These values can be obtained from low-pressure adsorption data or from solid gas chromatographic measurements, neglecting gas imperfections [271,272]. The necessary condition for the application of the virial description formalism is that sufficiently low-pressure can be obtained in adsorption experiments [36]. Thus, the virial formalism turned out to be a valuable method to investigate the effect of surface heterogeneity at low surface coverages [270].

The virial expansions in activity or density have the same form regardless if the adsorbent surface is homogeneous or heterogeneous. On the other hand, the values of the virial coefficients are changed. In terms of suitably selected virial formalism it is possible to obtain quite new insight into adsorption energy distribution [273] and topography of the solid surface [274,275]. The second and higher virial coefficients are defined by integrals that contain the distribution function. That is why the main problem in virial formalism on heterogeneous surfaces is to omit the numerical difficulties in evaluating the virial coefficients [276–278]. However, the main information on surface topography is contained by the higher solid–gas virial coefficients, and a few approaches have been proposed in literature

for their evaluation [276,277,279–281]. A promising way comprises application of gas–solid chromatography data to study low-pressure adsorption [282,283] to determine the virial coefficients. Some papers published present the possibility of evaluating energy distribution functions from gas chromatographic data [284,285].

This brief discussion shows that the virial description of adsorption on heterogeneous surfaces is very promising, but further studies in this field are expected to lead to even better results. They should provide a more accurate description of the true mechanism of adsorption from the gaseous phase [36].

A quite new opportunity that leads to new insight into the subject of adsorption on heterogeneous surfaces has appeared owing to the introduction of computer simulation methods (e.g. [286] and references therein) which are recognised as very powerful tools. Based directly on a microscopic model of the adsorption system, the computer simulation approach, both Monte Carlo (MC) as well as molecular dynamics (MD), can provide an exact, numerical solution of the model assumed. The most important input for computer simulation methods are suitable potentials that represent all types of interactions in the system. Moreover, the surfaces of any accepted structure and their properties can be numerically generated and fed into the computer. In terms of this approach, one can obtain much richer information than that available from usually laboratory experiment. Thus, in terms of MC and MD approaches it is possible to carry out ‘computational measurements’ of adsorption isotherms, adsorption isobars and adsorption isosteres, to calculate all types of adsorption heats and the heat capacity, to evaluate the local density profiles, radial distribution functions, structure factors, etc. The methods under consideration give a truly unique possibility to observe how the system evolves in time, changes its inner structure and what happens with every single particle. With regard to adsorption on heterogeneous surfaces, a new possibility arises to visualise how the spatial distribution of heterogeneities determines the shape of adsorption isotherms and that of all other thermodynamic properties. The results obtained by means of computer simulation methods can be compared with experimental data and with the forecast of different theoretical approaches. Owing to such comparison, experimental data may be correctly interpreted and theoretical models may be verified.

The principles of the computer simulation are very rigorously determined in terms of statistical mechanics and thermodynamics, and will briefly be presented in one of the later chapters of this review. A comprehensive monograph which presents the state of the art of achievements of computer simulation methods in surface science researches has been edited recently by Borówko [287]. The contributors to this book present in-depth analysis of advanced theoretical methods to describe the behaviour of fluids in contact with nanoporous, semiporous and porous solid surfaces.

4.1.2. Adsorption of gas mixtures

In the 1970s and 1980s there were also developed studies of adsorption from gas mixtures on the solid heterogeneous surfaces [288]. This phenomenon underlies a number of extremely important processes of utilitarian significance, e.g. separation

and purification of mixtures on a laboratory and industrial scale [289]. In spite of the impressive progress that has been made in improving new techniques for the measurement of adsorption of gas mixtures, they are still time-consuming experiments. On the other hand, measurements of single gas isotherms can be made easily and quickly by means of various adsorption techniques. Thus, predicting mixed-gas adsorption equilibria from the knowledge of single adsorption isotherms is of great, most practical importance and represents the main challenge to theories of adsorption from gas mixtures on solid surfaces. In many important technological processes it is essential to know the mixed-gas adsorption equilibria that correspond to a variety of technological regimes as well. Although, being in principle possible, it is in practice impossible to obtain the necessary knowledge of mixed-gas adsorption equilibria from mixed-gas adsorption measurements. This results from both most extended experiments are needed and from the fact that in those technological processes the physical regimes may change very quickly. It is important to use a fast method for calculating the mixed-gas adsorption equilibria. Thus, it is not surprising that in modelling industrial separation processes for gases by adsorption processes very simple isotherm equations have been used in the systems of differential equations that describe the dynamic separation of gases. However, the isotherm equations which have been used are that crude that they give rise to the following question: would it be possible in the present state of theory, to propose equations that are more accurate, yet simple enough to calculate quickly mixed-gas adsorption equilibria? To make the calculations accurate, the theoretical considerations have to take into account all the most important physical factors that govern the behaviour of adsorption systems. At present there are the following two factors: (1) the gas–solid interactions and their dispersion at various points on the real gas–solid interfaces called surface energetic heterogeneity; and (2) the interactions between the adsorbate molecules. The most advanced theories should introduce both of the above mentioned factors. Theoretical approach to adsorption of gas mixtures on heterogeneous solid surfaces is based either on the integral adsorption equation [290] or on the ideal adsorbed solution (IAS) theory proposed by Myers and Prausnitz [291]. Another approach proposed by Danner and Choi [292] deals with the combined effects of the dispersion in the gas–solid interactions and mutual interactions between adsorbed molecules. These combined effects can be handled theoretically by introducing certain effective activity coefficients in the adsorbed phase. A series of methods based upon solution thermodynamics is described in [293]. In consequence, for the same model of single-gas adsorption various expressions for mixed-gas adsorption were developed in terms of various theoretical approaches [294]. An excellent review on the subject under consideration has been presented by Rudziński and co-workers [294–296]. This review clarifies the justification as to how a choice of an isotherm equation for mixed gas adsorption is motivated by the physical picture of the adsorption system investigated.

4.1.3. *Adsorption of liquid mixtures*

From a technological point of view, beside adsorption from gas mixtures, that

from liquid mixtures is also important. We will dwell on the adsorption both from diluted solutions [297,298] and references therein) and from the solutions in the full range of their concentrations [13,15,16]. Such studies are of great importance in the industrial separation of liquid mixtures as well as in the environmental protection processes. Moreover, adsorption from multicomponent solutions is a basis for the theory of adsorption liquid chromatography [299].

The simplest description refers to single-solute adsorption [300–303]. Assuming high dilution of the solution, the interactions between the molecules of the dissolved substance and the solvent can be neglected, and the process can be described as in the case of single-gas adsorption. The description of multi-solute adsorption is more complex [304]. In terms of this approach some important expressions were developed and used widely for predicting the multi-solute adsorption equilibria by means of single-solute adsorption parameters [305,306]. We should mention here the possibilities of application of the so called n -dimensional integral equation in the thermodynamic description of adsorption from n -component diluted mixtures on heterogeneous surfaces, assuming an n -dimensional energy distribution function [307].

Considering adsorption from undiluted solutions and gaseous mixtures under high pressure, the phenomenon of competition among adsorbing molecules towards adsorption centres should be taken into account. In this case, the difference of adsorption potentials of adsorbate molecules plays a significant role and experimental isotherms have the character of excess isotherms [15]. A competitive adsorption process complicates the theoretical description and physical interpretation of adsorption energy distribution function. Moreover, adsorption of more than one type of molecules increases the number of parameters which must be taken into account by theoretical description of the phenomenon. In case of the relatively simple adsorption from a two-component solution over the full range of their concentrations at constant temperature, the process is determined by the following parameters [308]: (1) molecular interactions in the bulk phase; (2) molecular interactions in the surface phase; (3) interactions between the bulk and surface phases; and (4) molecular interactions at the solid/solution interface. In the case of adsorption from multi-component solutions and adsorption from gas mixtures, the description is largely complicated [309,310]. It should be emphasised that effects resulting from the surface heterogeneity, are sometimes compared quantitatively with those caused by intermolecular interactions of the adsorptive in its bulk phase [308]. The character and value of interactions mentioned under (4) depend on structural and energetic heterogeneity of the solid surface, which is characteristic of a great number of adsorbents used in practice.

In 1973, Coltharp and Hackerman [311,312] showed experimentally that adsorbent heterogeneity may determine the type and range of competitive adsorption from solutions on solids. In the same year, Rudziński and co-workers [313] published the first paper in the world literature in which the heterogeneity effects were described in a quantitative way for benzene adsorption from cyclohexane on silica gel. Their description was based on the patchwise model of heterogeneous solid surfaces. This paper became the basis to further investigations that dealt with

the determination of the distribution function from liquid phase adsorption data. Numerical methods for a determination of this distribution function were next elaborated by several authors [314–318]. Extensive studies of heterogeneity effects in adsorption from solutions on solids are still being developed [319–321], and they include investigations of the influence of different types of distribution functions on the shape of the excess adsorption isotherms [322,323], and the study of correlations between adsorption from gaseous and liquid phases [324,325]. Some authors considered the mutual role of adsorbent heterogeneity and molecular interactions in the adsorption process at the solid–liquid interface [308,326,327].

Until now satisfactory results were obtained with regard to:

1. single and multicomponent adsorption on heterogeneous solid surfaces [297,298];
2. adsorption from two- and three-component solutions of non-electrolytes on homogeneous and heterogeneous solid surfaces [308,328–330];
3. methods of determination of the capacity of surface phases formed on heterogeneous solid surfaces [331,332];
4. possibilities of prediction of adsorption from liquid and gas mixtures based on the measurements of individual isotherms of the components from the gaseous phase [294,295,324,325,333]; and
5. another important task was aimed at the concept of the global activity coefficients; this problem was solved by Dąbrowski and co-workers who were able to separate the non-ideality of the surface phase caused by intermolecular interactions from that generated by surface heterogeneity of the solid [334,335].

Very recently, a new approach to the determination of the surface phase capacity and the distribution function in liquid adsorption on heterogeneous solid surfaces has been presented [331,332,336]. This approach deals with a statistical analysis of the errors made by applying the Langmuir–Freundlich and exponential equations of the adsorption isotherms. It has been proven that such an analysis that is suitable for all types of excess experimental isotherms, gives an answer to the dilemma of the reliability of results obtained by means of the assumed adsorption model. On the other hand, during recent years an important contribution was made by Dekany and co-workers to the calculation of adsorption parameters that characterise the solid–liquid interface [337–341].

4.1.4. *Fractal approach to adsorption*

In the 1980s, a new trend of studies on adsorption started from the work by Mandelbrot ‘*The Fractal Geometry of Nature*’ [342]. This work opened new possibilities for the quantitative characterisation of geometric irregularities at the surface. In the classical meaning, a surface was assumed to be a two-dimensional matter whose geometrical irregularities present small deviations from an ideal arrangement. If these geometric irregularities show a spatial extension that is comparable with the size of the adsorbate molecules, one can speak of fractal surfaces [343,344]. This situation is adequate for several amorphous solid adsorbents and leads to numerous consequences of their adsorbing behaviour. The strictest conse-

quence is the loss of meaning of the concept of surface area which is replaced by the definition of the fractal surface itself. For a series of adsorbate molecules of different sizes, but with geometrically similar cross-sections, the apparent surface area of several solids (silica gels, active carbons, activated charcoals, crushed glasses, etc.) is connected with the effective cross-sectional area of the adsorbate molecule, a_m , by the relation: $A \propto \rho^{2-D}$, where $\rho = a_m^{1/2}$. Here, D is a non-integer number between 2 and 3, known as the fractal dimension. Its value varies from $D = 2$ for an ideal planar surface to $D = 3$ for a hypothetical porous solid with negligibly thin walls. Many methods have been developed in order to obtain the parameter D on the basis of mercury porosimetry, scanning electron microscopy and small angle X-ray diffraction as well as neutron-scattering measurements [344,345]. On the other hand, several methods have been proposed to understand the influence of fractal geometry of solid adsorbents on adsorption isotherms [346–352]. Some of them are simple and convenient since they require only one complete adsorption isotherm for a given solid to calculate the value of D [353,354]. Arguments were put forward against the assessment of the fractal dimension from experimental adsorption data [355]. Later their relevance was questioned [356].

It follows from the above considerations that the fractal analysis performed in terms of adsorption measurements, both from gaseous and liquid phases, could probably be a the next important tool for characterising surface irregularities. However, this way of research is new and still under development. It is too early to summarise its achievements now. Undoubtedly, the fractal analysis as applied to porous materials can provide important additional information to characterisation of adsorbent surfaces.

4.1.5. Kinetics and dynamics of adsorption

In the industrial usage of adsorbents, the time dependence of adsorption on solid surfaces is named as adsorption kinetics. The more general term ‘adsorption dynamics’ deals with the time evolution of adsorption processes in adsorbents and other industrially used units. With the development of the theory of equilibria of adsorption on heterogeneous solid surfaces, the theory of adsorption–desorption kinetics on heterogeneous surfaces was also developed. Adsorption kinetics is determined by the following stages: (1) diffusion of molecules from the bulk phase towards the interface space — so-called external diffusion; (2) diffusion of molecules inside the pores — internal diffusion; (3) diffusion of molecules in the surface phase — surface diffusion; and (4) adsorption/desorption elementary processes. In the case of sorption kinetics on microporous solids, a series of other mechanisms may additionally take place, *sui generis*. Diffusion in micropores carries the character of activated diffusion which usually, is described by specific solutions of Fick’s second law [357]. Before sorbing species may enter micropores, the surmounting (penetration) of surface barriers may be necessary [358]. Generally, it can be assumed that the total rate of the kinetic process is determined by the rate of the slowest process. However, multi-disperse models offer more accurate quantitative description [359]. The diffusion processes in multi-disperse

(multi-porous) solids are almost always complicated by those molecular sieve and activated diffusion effects. In the former case, the adsorption into the smaller pores is excluded, because adsorbate molecules are too large to enter these smaller volume elements. Activated diffusion takes place when the dimensions of the adsorbate molecules are only slightly smaller than the pore diameter. Consequently, at low temperatures the adsorbate molecules have insufficient kinetic energy to enter the pores. The activated diffusion is confirmed when, by measuring the isotherm at higher temperature, the equilibration time is reduced. In these cases, the above-mentioned surface penetration resistances may play a rate determining role. For non-porous and macroporous solids the internal diffusion may be neglected. In this case, the adsorption kinetics is determined by external diffusion and molecular adsorption/desorption processes. The Langmuirian kinetics, based on the ideal monolayer adsorbed model, proved to be deceptive for most real adsorption systems that include structurally (high porous) and energetically heterogeneous solids. On the other hand, the adsorption/desorption kinetics theories are technologically extremely important, because the diffusion of adsorbed particles on solid surfaces is a phenomenon of great importance in catalysis, metallurgy, microelectronics, material science and other numerous scientific and technological applications. As for the matter of catalysis since the adsorption of reactants and desorption of products are fundamental steps of heterogeneous catalysis, there is a need to understand the kinetics of adsorption/desorption phenomena on heterogeneous surfaces.

In the 1970s and 1980s in the majority of papers devoted to the adsorption kinetics, the models of mass transfer kinetics were examined [4,159,360]. These models took into account external, internal and surface diffusion of adsorbate molecules. However, in terms of mass-transfer kinetics, some authors investigated the influence of the energetic [361,362] and structural heterogeneity [363,364] of solid adsorbents. Jaroniec [365] discussed the adsorption and desorption rates for kinetics of localised adsorption of single gases and their mixtures on energetically heterogeneous solid surfaces, assuming discrete, continuous distribution of energies among adsorption sites. In terms of simple considerations, he derived both the kinetic and various equilibrium adsorption isotherms. Czarniecki and Jaroniec proposed the stochastic modelling of adsorption kinetics of localised and mobile adsorption on homogeneous and heterogeneous surfaces [366–368]. Their approach based on the Monte-Carlo technique, allowed to take into account the following aspects [369]: (1) the monolayer and multilayer character of surface phase; (2) the localised and mobile character of the surface phase; (3) the association of molecules in the surface phase; (4) energetic heterogeneity of the adsorbent surface; (5) the type of topography of adsorption sites; and (6) surface diffusion in the adsorbed phase. The above investigations were performed for adsorption of single gas, gas mixtures and liquid mixtures.

The other way of investigations of adsorption/desorption kinetics on solids is connected with the famous and commonly used empirical expression known in literature as the Elovich equation [370,371]. The excellent work on application of

this formula for describing single-component adsorption/desorption kinetics on heterogeneous surfaces was presented recently by Cerofolini [372].

Quite new perspectives for the investigation of kinetics and surface diffusion processes on flat (energetically heterogeneous) and porous (structurally heterogeneous) solid surfaces are connected with molecular modelling of adsorption phenomena [373]. Moreover, the invention of atomic force microscopy (AFM) and scanning tunnelling microscopy (STM) gave excellent sources of information on the mechanistic models that can be accepted in computer simulation. A comprehensive overview of the state of the art of research in this subject was presented in the monograph: *Equilibria and Dynamics of Gas Adsorption on Heterogeneous Solid Surfaces* [374]. The relevant states of the art articles were recently published by Ruthven [375], Nicholson [376], Gubbins [377] and Do [378]. This last monograph covers topics of equilibria and kinetics of fluid adsorption in porous media.

As far as adsorption kinetics of multi-component mixtures by microporous materials such as zeolites are concerned, significant contributions made by Bülow and co-workers ought to be mentioned [379–382].

The above discussed topics deal only with the some important features of physical adsorption on heterogeneous surfaces from gas and liquid mixtures. To give a detailed account of all fundamental theories and descriptions, would require a whole book or books. The interested readers are advised to consult several already available review articles ([13,15,18,139,219–221,286] and references therein) as well as a number of excellent monographs ([218,237,287,374] and references therein).

4.1.6. *Molecular modelling and its relevance to adsorption phenomena*

During the last two decades the methods of molecular modelling of surface and interface phenomena have developed extensively [383]. On the other hand, the term ‘atomistic computer modelling’ or ‘atomistic simulation’ is widely used. This term deals with the computational methods that are based on first-principles of quantum mechanics and attempt to solve the Schrödinger equation for the system modelled. The above methods based on fundamental physical constants are independent of specific atoms or materials and, thus, can be applied to any system irrespective of availability of experimental data or not.

The methods under consideration are based on both Hartree–Fock and quantum local density functional (LDF) theories applied mainly to the study of new materials to predict their properties prior to any synthesis. The results allow for some new insights into materials’ behaviour on the atomistic level which are difficult or impossible to obtain otherwise [384]. Despite the continuing growth in computer power, the wide use of the atomistic computer modelling is rather limited [383], and there it appears an important role for interatomic interactions techniques including minimisation, Monte Carlo (MC) and molecular dynamics (MD) methods. In these methods, the interactions between atoms are described by simple analytical equations that contain attractive and repulsive terms with parameters chosen to reproduce experimental or quantum mechanical *ab initio* data. Thus, these methods named as ‘molecular modelling techniques’ refer to both approxi-

mate methods of statistical thermodynamics and molecular computer simulations methods [385]. They have emerged as an efficient tool for improving the fundamental understanding of basic microscopic phenomena and for helping to solve industrially relevant problems with regard to wide fields of chemical and physico-chemical processes [386]. Starting from the atomic scale, molecular modelling is the appropriate tool to develop a qualitative and quantitative knowledge of structure–properties relationships in a wide range of systems like molecules, bulk phases (gas and fluid) and interfaces [35,387–392]. One of the great advantages of molecular modelling of surface phenomena includes recognising and retrieving useful or even predictive information about the system investigated. When regarding complex molecular systems like porous and heterogeneous solids being in contact with fluids, the experimental studies have been preceded by the theoretical ones [393,394]. Computer modelling may also become a very promising method for fast development of industrial separation processes [395,396]. Gubbins showed [395] that the molecular modelling methods are useful for determining the effects of pore size and shape, temperature and other variables on the selectivity adsorption and its maximum effects. As programming technologies improve and computational power increases, the methods under consideration will be increasingly used as an addendum to experiments.

The classical models of adsorption processes like Langmuir, BET, DR, or Kelvin treatments and their numerous variations and extensions, contain several uncontrolled approximations. However, classical theories are convenient and their usage is very widespread. On the other hand, the aforementioned classical theories do not start from a well-defined molecular model, and the result is that the link between molecular behaviour and macroscopic properties of the systems studied are blurred. The more developed and notable descriptions of the condensed systems include lattice models [397] which are solved by means of the mean-field or other non-classical techniques [398]. The virial formalism of low-pressure adsorption, discussed above, the integral equation method and perturbation theory are also useful approaches. However, the state-of-the-art technique is the density functional theory (DFT) introduced by Evans [399] and Tarazona [400]. The DFT method enables calculation of the equilibrium density profile, $\rho(\mathbf{r})$, of a fluid that is in contact with the solid phase. The main idea of the DFT approach is that the free energy of an inhomogeneous fluid which is a function of $\rho(\mathbf{r})$, can be expressed by a sum of a hard-sphere short-range contribution and a longer-range attractive force contribution. The equilibrium density profile, $\rho(\mathbf{r})$, is obtained by minimisation of the free energy. Once $\rho(\mathbf{r})$ is known, it is possible to obtain all macroscopic information — like adsorption isotherm, density and relevant thermodynamic functions — about the adsorption systems studied. DFT can be considered as a useful method for investigating systems of simple geometry as well as pure and mixed fluids composed of spherical molecules [385]. For these systems it is possible to explore a large number of system variables relatively quickly and efficiently, such as pore sizes and pore shapes, solid–fluid interaction parameters, temperatures, concentrations, etc. [401]. The most advanced form of this theory is the so-called non-local density functional theory (NDFT) [402]. NDFT has been used for

describing fluids confined in narrow pores [403,404], and for analysing pore-size distribution of microporous carbons [405]. The main disadvantage of the density functional theory refers to its difficulty, to be applied to complex systems including fluids consisting of non-spherical molecules, pores of mixed geometry or heterogeneous surfaces. In this case, other ways of molecular modelling, namely computer simulation methods seem to be more adequate [385,406,407]. Nonetheless strong development is possible as shown recently by Neimark and co-workers [408,409].

One of the main reasons for using computer simulations is the fact that they eliminate inaccuracies that result from approximate statistical thermodynamic methods. In terms of computer simulations methods, it is possible to investigate systems that are not subject to analytical description. As the methods under investigation can be used to study complex systems, they provide standard data for verification of approximate theories. Moreover, they allow for a comparison of molecular models with experimental data as well as to assess correctness criteria for their choice. Thus, the molecular simulation methods are useful for testing the exactness of assumed intermolecular potentials, to validate approximate statistical thermodynamic theories and to explore systems under conditions and with a level of detail which are hard to achieve by conventional experiments.

As an example, the internal diffusion phenomenon can be named which cannot be observed in direct laboratory experiment but can be ‘observed’ and assessed quantitatively using computer simulation methods [410]. During the last few years, the revolutionary progress in the field is connected with developing new algorithms and with striking increases in computing speed.

The starting point of molecular simulation methods is — as in the density functional theory — the well-defined microscopic description of the system studied. This microscopic (molecular) specification includes: (1) the equations of statistical thermodynamics that describe the fluid–fluid and solid–fluid interactions; and (2) the molecular model of solid adsorbent. This model should take into account all possible and reliable information on the solids, most of which can be developed from various modern surface science techniques [411,412]. For instance, some important data on bulk crystalline structures are given by X-ray diffraction, neutron diffraction methods, nuclear magnetic resonance (NMR) or high-resolution transmission electron microscopy (HRTEM). Scanning tunnelling microscopy (STM), atomic force microscopy (AFM) as well as small angle X-ray scattering (SAXS) are valuable sources of information on the topography of a solid surface [413]. For solving the equations of statistical mechanics that correspond to the molecular model of the system, two methods are usually used: Monte Carlo (MC) and molecular dynamics (MD). The MC method was developed by Metropolis et al. in 1957 [414] but the first molecular simulations were performed by Alder and Wainwright [415] in the Livermore Laboratory in California [416]. The main idea of the MC approach refers to estimating the configurational contributions to the thermodynamic quantities of a given statistical–mechanical system, which are calculated by averaging over all accepted configurations. The MC method allows for a generation of different types of statistical ensembles according to the equilibrium properties of the system which were sought [377]. For instance,

isosteric heats of adsorption are derived from the canonical ensemble, but adsorption isotherms and fluid phase equilibria from the grand canonical and Gibbs ensembles, respectively. As follows from the above considerations, the MC method gives configurational equilibrium properties of a system investigated. In the MD method, the molecules are dislocated owing to their own intermolecular forces. The trajectories of molecules are calculated by direct solution of Newton's equations of motion, but desired properties of a system are assessed by averaging over the trajectories. Thus, contrary to the MC approach, the MD method allows to obtain both equilibrium and dynamic properties of the system. Therefore, MD simulations are very useful for studying diffusion effects and phase separation phenomena. The detailed discussion of advantages and disadvantages of MC and MD methods for solving specific problems of the surface science has been presented recently by Gubbins [385]. He also showed the relevant point of view on applications of the molecular modelling methods toward selective adsorption of mixtures of great industrial importance.

To give a brief description of numerous applications in which molecular modelling of surface phenomena is a significant feature, would require a book in itself. Some examples were included in the section that deals with heterogeneous catalysis, but others have been presented above. Let us attempt to summarise the considerations on the subject as follows:

- Molecular simulation methods are of great importance to computational studies on the design of new synthetic sorbents and catalysts like zeolites [182,417], aluminophosphates [181,418,419], aluminosilicates [420], nano- and mesotubes [421,422], fullerenes and heterofullerenes [423–425], pillared-clays [426,427] and other disordered porous solids [428–431]. The above solid materials are very important in selective adsorption, catalysis and separation technology.
- In terms of molecular modelling of adsorption phenomena the following problems were examined: adsorption of simple fluids and/or their mixtures on/and in heterogeneous solid phases like zeolites [432], porous carbons [375,376,433], carbon nanotubes [181,434,436] and other porous materials [406]. Quite recently, results were reported on molecular simulations of adsorption phenomena on new types of heterogeneous surfaces including porous structures [437,438]. Adsorption of fluids on amorphous solid surfaces was also investigated [391,439]. An important part of the aforementioned studies deals with dynamic aspects like kinetics (diffusion) and phase transitions [287].
- Simulation methods are very efficient for studying the effects of surface heterogeneity on equilibrium and kinetics of fluid adsorption, thermal desorption, surface diffusion and surface reactions [439–441] (see also ref. [374] and references therein).

Although we restricted ourselves to the selected problems in the molecular modelling of adsorption phenomena it should be stressed that the topic is vast.

Finally, some difficulties should be pointed out which are connected with practical aspects of the molecular modelling approach. The main difficulty refers to

a lack of definite knowledge of the structure of solid adsorbents and inadequate or improper experimental data that can be used to refine the models. In the case of microporous crystalline materials, like zeolites, aluminophosphates and others, their structure can be exactly determined by X-ray or neutron diffraction. However, the morphology of amorphous materials, such as activated carbons, oxides or silica gels is still poorly recognised. In this case, the simple model structures in which the pores are represented as slits or cylinders, are usually applied. The second main disadvantage of molecular simulation is that our knowledge on intermolecular forces is still inadequate [36]. In the article on atomic calculations of the Henry constants in A zeolite which was published in 1975, Derrah and Ruthven wrote [442]: ‘the practical limitations of this approach arise not from the difficulty of performing such calculations but rather from the present unsatisfactory state of knowledge of intermolecular forces’. Unfortunately, 25 years later the subject still needs better understanding. Evidently, strong advances have been made in this field as well as in the simulation methods and at present more complex systems can be simulated. It is clear that quantum chemistry *ab initio* methods should be developed to increase the accuracy of calculations of the solid/fluid interaction potentials for all types of adsorption systems. The third disadvantage of molecular simulations is the fact that very extended computing time may be needed for complex systems. For this reason, the dynamic processes that are slow, e.g. desorption from strongly binding sites, activated diffusion effects or phase separations at high density in the associated pore structures, are difficult to study. This problem will be solved by further improvements in computing power. Finally, *the principal difficulty in the field of development of molecular modelling method is connected with a still poor interaction between modelling and experiment* [385]. The more complex and realistic models that arise from molecular modelling should be tested by means of more accurate experimental data interpreted in terms of well-posed theories. *Thus there is a need for close co-operation between theoretical and experimental groups, in which the experiments and models are designated to complement each other.*

4.1.7. Future trends and prospects

It follows from the above considerations that at present and in the near future the development of adsorption will be stimulated by:

- development and application of widely understood modern techniques to study adsorption experiment; these methods should be applied for precise measurements of both adsorption isotherms and heats of adsorption [443,444]; the other structural techniques such as STM, AFM, XRD, FTIR, various kinds of NMR should be also contributed to our understanding of the structure of bulk solids, surfaces and interfaces [393];
- development of computational material science to design new types of adsorbents and catalysts ([445] and references therein); in the future the combination of advanced simulation techniques and experimental databases together with artificial intelligence [446] will open new, exciting perspectives for development

of computational material science — a strategic technology for the 21st century;

- development of molecular modelling methods of adsorption which depends on progress in software, hardware and in increasing the accuracy of quantum chemistry *ab initio* approaches for calculations of the solid/fluid interaction potentials for all adsorption systems;
- another area for future work is making careful comparison of the model computational results with experimental ones, particularly for explaining the microscopic details of adsorption phenomena;
- one can suppose that for the complex systems that is: fluid/solid including amorphous solids with complex porous structures and complex fluids or their mixtures as H-bonding or associated mixtures, mixtures composed of non-spherical species, simple and realistic phenomenological models of adsorption systems will be still of great practical importance; such models cannot lead to too complicated equations because their practical applicability is doubtful; the nearest perspective dealing with phenomenological models will include the following:
 - making the uniform thermodynamic description of adsorption to predict adsorption isotherms from gas and liquid mixtures based on single gas isotherms;
 - simultaneous studies on heats and adsorption isotherms at different temperatures; and
 - preparation of a theoretical approach making it possible to predict adsorption isotherms at different temperatures from the isotherm determined at the given temperature.

One ought to point out here the noteworthy unified descriptions of physical adsorption both from the gas and liquid phases on solids [209]. Quite recently, an uniform description and uniform interpretation of gas–solid adsorption has been proposed by Tóth [447]. Such uniform description developed in terms of classical thermodynamics opens a new possibilities for easier understanding of the complex adsorption phenomena and modifies our old views of classic models of physical adsorption.

5. Basic types of industrial adsorbents

As follows from the aforementioned considerations, development and application of adsorption cannot be considered separately from development of technology of manufacture of adsorbents applied both on the laboratory and industrial scales. These sorbents can take a broad range of chemical forms and different geometrical surface structures. This is reflected in the range of their applications in industry, or helpfulness in the laboratory practice. It is comparable to the variety of adsorbents one finds in various environmental applications as well [448].

Table 3
Basic types of industrial adsorbents

Carbon adsorbents	Mineral adsorbents	Other adsorbents
Active carbons	Silica gels	Synthetic polymers
Activated carbon fibres	Activated alumina	Composite adsorbents:
Molecular carbon sieves	Oxides of metals	(complex mineral-carbons,
Mesocarbon microbeads	Hydroxides of metals	X-elutrilite; X = Zn, Ca)
Fullerenes	Zeolites	Mixed sorbents
Heterofullerenes	Clay minerals	
Carbonaceous	Pillared clays	
nanomaterials	Porous clay hetero-structures (PCHs)	
	Inorganic nanomaterials	

Since our early history, active carbon was the first widely used adsorbent. Its application in the form of carbonised wood (charcoal) has been described as early as 3750 BC in an ancient Egyptian papyrus. To give a detailed account on this comprehensive subject would require a whole book. Recently, excellent monographs and review articles on activated carbon, its historical production, structure, characterisation and applications were published ([142,449–454] and references therein), and the interested readers are advised to consult the suitable literature. The same refers to other adsorbents of great practical importance (Table 3).

In different periods of time, development of the adsorption technique was based on various types of adsorbents: before World War I on carbon adsorbents, during the period between World War I and World War II on active carbons, silica acid gels and aluminium oxides, but after World War II revolutionary progress was made owing to discovery and application of synthetic zeolites [90,91]. At present, besides 40 natural zeolites, there are recognised crystallographically approximately 120 synthetic structures. Many more are described but not yet deciphered by suitable methods of structural investigation.

Adsorbents and catalysts dealing with new porous materials are recommended for ecologically friendly processes, formulation of criteria for estimation of acceptability of many current technologies and important ways of sustainable development. Thus, we only mention here some most important aspects aimed at novel porous materials, both inorganic as well as carbonaceous ones. Polymer-based adsorbents are also briefly mentioned.

Porous solids are a rapidly growing group of inorganic and organic compounds. Research into their synthesis and fundamental nature promises great potential for innovation. Major progress has been made for microporous solids, known as *molecular sieves*, which are mainly used as catalysts and adsorbents for fluids separation and purification. Some of the novel potential applications of molecular sieves include membranes, chemical sensors, storage materials for, both, various compounds and information, as well as semiconductors. Other uses, such as, for high-tech materials in nano-chemistry and nano-physics, are expected to be transferred into practice soon. Their utilisation in traditional areas such as ion-ex-

change, drying, improvement of animal food, detergent production is also anticipated [455–457].

The main class of microporous sorbents are zeolites which comprise, according to a recommendation of Structure Commission of the International Zeolite Association, not only aluminosilicates, but also all other interrupted frameworks of zeolite-like materials, e.g. aluminophosphates, provided that the framework atoms other than oxygen are tetrahedrally co-ordinated at least in the calcined form. There is a tremendous versatility in chemical composition of molecular sieves. By the end of August 1999, approximately 40 naturally occurring species and at least 115 synthetic structures were known precisely [458]. However, more than 200 still undecoded novel zeolitic structures may have already been synthesised. A careful estimation may indicate that annually some 15 novel structures were synthesised [458], but only three–five of them were decoded. *The discovery of novel molecular sieve structures has been so prolific, that a time lag of several years usually occurs between the discovery of a species and its crystallographic definition.* Proprietary interests of industrial companies may also prevent disclosure of new structures and modifications as well as related information. Many hypothetical molecular sieves which obey quantitative topological and chemical rules as well as crystallo-chemical laws, are yet to be synthesised. This vision challenges zeolite chemists all over the world. Besides zeolites, a large and still increasing number of other porous solids are known (Table 4). Very recently, many novel micro- and mesoporous metallorganic structures became known. These inorganic compounds with ordered micro-space networks of secondary building units which allow design of porous systems with cross-sections of molecular dimensions, e.g. between 0.3 and 1.5–2 nm known to date, were mainly used as selective adsorbents and catalysts [459].

With respect to catalysis, hundreds of new reactions proceeding over molecular sieves were discovered, and the concept and applications of shape-selective catalysis are well recognised. Dozens of commercialised petroleum processing and petrochemical processes, which save raw materials and contribute to the preservation of the environment, have been introduced into practice. However, only a minority of new materials available today have been tested with respect to their catalytic properties. On the other hand, catalysis is still the main goal of zeolite research directed towards application. Here, there is great potential for the use of zeolite catalysis in the production of fine chemicals and perhaps as enzyme mimics. Large pore molecular sieves with a pore width > 1 nm may become important for processing of heavy petroleum fractions as well as for separation and purification of biochemical products. In the near future, we will probably witness the production of optically active compounds over zeolite catalysts.

Moreover, the identification of adsorption properties of microporous solids with respect to their potentials use in sorptive separation and purification processes, is far beyond the actual availability of these new adsorbents. Strengthening the efforts in this field should lead to an intensification of established processes, e.g. PSA (see Section 6) for various purposes of gases separation and purification. Novel separations become possible by means of tailoring both the adsorbent properties to the physico-chemical nature of mixture components (fine tuning) and

Table 4
Chemical diversity of molecular sieves and related nanoporous materials

Molecular Sieves									
Silicas	Alumino-borates	Metallo-silicates	Metallo-sulphides	Metallo-aluminates	Metallo-cyanates	Elemento-phosphates	Stanno-titanates	Gallo-germanates	Other
Silicalite	Metallo-alumino-silicates	Metallo-silicates	Metallo-silicates	Germano-aluminates	Alumino-phosphates	Alumino-phosphates	Metallo-alumino-phosphates	Inorganic pillared clays	Molten salt activated carbons
Dealuminated Y-type zeolite	Multi-metallo-silicates	Alumino-silicates (zeolites)	Beryllio-silicates	Beryllio-silicates	Elemento-alumino-phosphates	Elemento-alumino-phosphates	Silico-alumino-phosphates	Substit. organic pillared clays	Porous polymeric adsorbents
Micro-mesoporous silicas MCM-41	Other	Stanno-silicates	Boro-silicates	Boro-silicates	Metallo-alumino-silico-phosphates	Metallo-alumino-silico-phosphates	Elemento-alumino-silico-phosphates	Carbon molecular sieves	Buckminsterfullerenes
Other mesoporous silicas		Titano-silicates	Chromo-silicates	Chromo-silicates	Dimetallo-alumino-silico-phosphates	Dimetallo-alumino-silico-phosphates	Beryllio-phosphates	Layered Inter-calates	Carbon nanotubes
Other		Vanado-silicates	Ferri-silicates	Ferri-silicates	Other	Other		Polyacid oxometallates	Porous glasses
		Gallo-silicates	Other	Other				Amorphous metal oxides	Other

of matching the technological conditions to the differing adsorption kinetic properties of mixture components. New applications, e.g. to separate and to purify fine chemicals and bio-technological products can be recognised. New technological principles such as the simulated counter-current moving bed, the adsorption hybrid ones with respect to permeation, distillation and catalysis, etc., can both be improved and transferred into wide practical use.

Beside adsorptive separation processes, membrane-based gas separation processes have been treated increasingly world-wide over the past decade. Achievements that have been gained not only in the field of polymeric membranes but also in that of inorganic, especially microporous ones, have promoted the current strong interest in membrane-based gas separations [460]. The promise of steady progress toward removing remaining limitations suggests the likelihood of its strong long-term growth.

The most representative porous solids are activated carbons [449–454] and zeolites [456,461–463,465]. Recently, the research achievements on this subject are well represented by *pore size engineering* [464]. This approach is based on changing raw materials and preparation conditions to enable to creation of structurally different forms of the same basic porous solid. In terms of pore size engineering one can obtain a wide class of nanoporous materials that have different pore geometry and chemical nature (Table 5). Nanoporous solids are very popular in science and technology due to potential applications envisioned for various separation, purification and catalytic processes [142]. On the other hand, computational studies on the design of new synthetic sorbents for selective sorption of various molecules have been developed to accelerate the progress in nanopore fluids chemistry [465].

Astonishing developments take place in the field of carbon-based materials such as carbon molecular sieves (CMS) and microporous/mesoporous carbons as of the MAXSORB type that reach the theoretically possible limit of specific surface area, approaching 4000 m²/g; but also other products made from mesocarbon microbeads (super activated carbon) or representing activated carbon fiber [466,467].

Discovery of molecular carbon structures as fullerenes and heterofullerenes [468–470] and carbon nanotubes [471] has boosted search for new selective adsorption applications of such materials. Carbon nanotubes represent a new generation of nanoporous solids which may provide great potential for selective adsorption and shape selective separation [435,436]. They may show capability of adsorption of noble gases and of air separation (capturing of both helium and neon by fullerene cages at high temperature) or related carbon ‘nanotubes’, single-walled and multi-walled, synthesised with 2–20 nm diameter and several mm in length [472,473] and which could function as capacitors in memory devices, as transistors in switching circuitry or as ‘micro wires’ (recently, it has been reported [474] that in the presence of liquid lead the capped nanotubes’ ends can be opened and filled with molten material). The nanotubes may rearrange into ‘onion’ like multi-walled balls for energetic reasons. On the other hand, the shells can be removed step-wisely by appropriate thermo-chemical treatment to leave walls of single graphite layer [475–477]. The interesting magnetic properties of carbon nanotubes

Table 5
Nanoporous systems [465]^a

Compound	Surface component	Pore shape	Pore width (nm)
Zeolite	Si, Al, O	Cylinder, cage	0.3–1
Aluminophosphate ALPO [SAPO: Si, Al, P, O; TAPO: Ti, Al, P, O; FAPO: Fe, Al, P, O, etc]	Al, P, O	Cylinder	0.8–1.3
Aluminiummethyl phosphonate	Al, CH ₃ PO ₃	Cylinder Triangle prism	< 1
Mesoporous zeolite [Al, Zn, Ti, Zr, W, Pb etc can be doped]	Si, O	Cylinder	2–10
Activated carbon fiber	C	Slit	0.6–1.3
Carbon aerogel	C	Intergranular void	5–30
Activated carbon aerogel	C	Slit + void	1, 5–30
Pore-oriented carbon film	C	Slit	< 1
Carbon nanotube	C	Cylinder	> 2
Carbon mesotube	C	Cylinder	30–200
Graphite intercalat.comp.	C, K, etc.	Slit	< 0.5
Microporous BN	B, N, H	Slit	< 1
Pillared clay	Si, Al, O	Slit	> 0.5
Porous glass	Si, O	Cylinder	5–10 ⁴
Organic metal complex	Organic group	Void	Variable

^aThe term: *nanopore* is not recommended by IUPAC, but it is often used for pores whose width comprises micro- and mesopores, i.e. ≤ 50 nm.

became a topic of intensive research [478]. The interest is to computer design their effective molecular sizes for bulk separations of mixtures of hydrocarbons molecules of industrial importance [181]. The selective adsorption of molecules over ceramics and extraction with supercritical fluids is also an emerging technology [465].

Zeolites are the only existing crystalline materials with a well defined pore structure in the microporous range. They exhibit unique features. Due to the presence of aluminium in the structure, many zeolites have strong acid sites at their surface, making them superior cracking catalysts. A product selectivity in the catalytic reaction is ensured by the microporous matrix of the catalysts. Steric phenomena are very important in zeolite catalysis, and a term ‘shape selective catalysis’, is coined to describe these effects. Because cations contained by most of known zeolites, the charge-compensating cations are free to migrate in and out zeolite structures, these solids are good ion-exchangers. This property can be used to introduce different cations in the structure, creating selective sites for adsorption purposes or catalysis. Their narrow pore size and tuneable affinity for certain molecules make them ideal adsorbents for selective purification of gas mixtures or for to encapsulation of hazardous compounds. Zeolites are characterised not only by high selectivity (selective separation mechanism), but also by the ability to separate substances based on differences in sizes and shapes of molecules (steric

separation mechanism). Consequently, the species with a molecular diameter which makes them too large to pass through a zeolite pore are effectively 'sieved'. Adsorption processes based on molecular sieving and selectivity are always reversible in theory and usually reversible in practice. This allows the zeolite to be reused many times, cycling between adsorption and desorption step of actual processes. This accounts for the considerable economic value of zeolites in adsorption applications.

Internal modification of zeolite could be based on chemisorption of silane or diborane which changes permanently their pore structure. The pore size reduction can be tuned by changing the modification conditions. Internal modification of zeolites as mentioned above — carried out by subsequent hydrolysis of the chemisorbed hydride groups — can also be applied for encapsulating gas molecules in zeolite channels. The capsules are homogeneous and stable towards acids, mechanical grinding and γ -irradiation. By controlling the pore size reduction, the thermal stability of zeolites can also be controlled. To control the pore-opening size without affecting the internal pore systems of the zeolite, modification can be performed using modifying agents with a molecular size larger than that of the zeolite pore so that they cannot enter the pores, and they interact with the external surface only. The deposition of silicon dioxide at the external surface of the zeolite reduces the size of the pore opening without changing the internal properties of the zeolite. This way, surface barriers as mentioned above can be created which allow for development of new methods of sorption preparation in the kinetic regime. Depending on the degree of the silicon dioxide deposition at the zeolite crystals the adsorption equilibrium behaviour also can be influenced.

A new family of mesopores materials — the so-called MCM materials (Mobil Composition of Matter) were developed by Mobil Oil Corporation which proposed a revolutionary synthesis method to obtain such materials that comprise strictly uniform pores [174,479]. In general terms, those materials were synthesised by means of template mechanism. An organic surfactant — like an alkyltrimethylammonium bromide — in an aqueous medium forms rod-like micelles which are used as templates to form two or three monolayers silica or alumina particles encapsulating the micelles external surface. By removing the organic species from well ordered organic — inorganic condensed phase, a porous silicate or alumina material with uniformly porous structure remains. The mesopore size can be controlled by the molecular size template of the surfactant. Several structures can be prepared in this way, but two types of them have gained widespread interest, i.e. MCM-41 with hexagonal array of uniform cylindrical channels and the cubic MCM-48 species [479–483] which has a random pore structure.

The other commonly applied inorganic sorbents are silica gels [484–487], activated alumina [488–494], oxide- and hydroxides metals [495–499] and clay minerals [177,500–507].

Another exciting class of new porous materials are pillared clays (PILCs) [178,179,503] developed from clay minerals [177,500]. The original clays — very useful materials for adsorption, catalysis and ion-exchange — have little the permanent porosity [500–502]. This problem has been resolved by intercalation of

stable pillars (e.g. cations of Mg, Mn, Fe, Al, Zr, etc.) or mixed oxide pillars between the layers [504–508]. The achieved porosity makes the pillared clays very attractive for adsorption purposes [503,507,508]. The other very useful group of new inorganic materials represent the so-called porous clay heterostructures (PCHs) [509]. Their synthesis represents a symbiosis of the MCM technology and the PILC technology. Recently, attempts were made to perform the PILC synthesis with an entirely new dimension. Instead of using non-porous pillars, as in the case of conventional pillars, MCM-like structures were synthesised *in between* the clay plates. The above new porous materials exhibit a large surface area and a combination of micro- and mesopores that could be tuned by on a suitable choice of synthesis procedure and surfactants.

Other inorganic adsorbents such as well-known microporous glasses (particularly ‘Vycors’, semicrystalline glasses) [510] as well as novel materials such as polyacid oxometalates [511,512], hexacyanometalate compounds and related structures serve as a remarkable oxygen adsorbents [513,514]. Brucite-type double layered structures, that show both micro- but mainly mesoporosity, but also carbon-metal cage molecules, so-called ‘met-cars’ may possess intriguing physical and chemical properties to be utilised in future [515].

The milestone achievement in the preparation of novel porous inorganic materials like glasses and ceramics is presented by the *sol-gel technology* [516–519]. In this new technique, the high-temperature heating procedures were replaced by polymerisation and coagulation of inorganic and organometallic compounds at room temperature. At present, almost all of the important inorganic oxides can be prepared via sol-gel processes [520,521]. The technology of manufacturing optical fibre glasses is also based on the sol-gel technique. The same content is true of ceramic membranes [516,517]. In adsorption processes a significant role is also played by microporous glasses sorptive properties of which are similar to those of gels and silica zeolites, however, the area of their application is wider. Microporous glasses may be used as semi-permeable membranes for the separation of liquid and gaseous mixtures, as well as gel filling in chromatography. Because of their high silica content, they may find application in chemical, metallurgical, electrotechnical and other industries [522]. There exists also the possibility to make use of these glasses in biochemistry, e.g. for long-lasting storing of enzymes or as protein testers that captures the conformation anomalies and contribute in this way to find clinical and diagnostic applications. On account of their sorptive properties, microporous glasses represent an excellent material for storing high-energy radioactive waste products in nuclear power engineering and for bounding toxins in natural environmental [523].

A comprehensive review related to adsorption on new and modified inorganic sorbents was presented recently in the monograph [524].

Strong efforts are directed on the development of novel polymer-based adsorbents, as polymeric molecular nanotubes, so-called ‘molecular necklaces’, with an internal diameter of 4.5 Å being significantly smaller than that of carbon nanotubes with diameters ranging from 10 to 300 Å. The former were synthesised by stringing together hollow molecular ‘beads’ on a polymer ‘string’ [525,526]. Such

tubes might be usable as catalytic hosts or as a novel form of separation *media* for chromatography and filtration. Other polymeric adsorbents have reached large-scale manufacture scale, e.g. Dowex MSC-1 materials or the Amborsorb-types. These represent carbonaceous (pyrolyzed) adsorbents of a similar chemical origin, which allow for specific adsorbent–adsorbate interactions due to different functional groups attached [527,528]. Companies with expertise in preparing polymeric membranes for permeation purposes seem to transfer their experience into the adsorbent field, thus, exploring possible applications.

A fundamentally important feature of industrial sorbents is their high porosity and usually high surface as well as specific sorption sites. That is why their most important characteristics deal with total pore volume, pore size distribution over the pore diameter and the specific surface area. Other features of practical importance like bulk density, crush strength and attrition resistance have been presented elsewhere [130]. A greater part of solid adsorbents of significant industrial applications possesses a complex porous structure which consists of pores of different sizes and shapes. Of the greatest importance are micropores which give a source of a considerable increase of adsorption capacity because their entire accessible volume can be considered as the adsorption space. Adsorption in micropores is essentially a pore-filling process in which their volume is the controlling factor. In contrast to micropores, for macropores and mesopores the layer-by-layer adsorption mechanism is accepted.

Application of solid adsorbents and catalysts requires their many-faceted characterisation which comprises determination of their chemical composition, crystallographic and geometrical structure, surface and mechanical properties, and the energy distribution functions as well as the shape and size distribution of the pores within the materials. The former functions characterise a global energetic heterogeneity of solids. Their physical interpretation is rather complex, but when associated with additional independent measurements such as calorimetric, spectroscopic and other ones, it gives valuable details on the correlation between the energy distribution of adsorption sites and their chemical nature [219]. Various modern techniques provide direct information about physicochemical properties of these solids [130]: electron and scanning microscopy, X-ray diffraction and X-ray spectroscopy, Auger electron spectroscopy (AES), Raman spectroscopy, small angle X-ray spectroscopy (SAXS), nuclear magnetic resonance (NMR), temperature-programmed desorption (TPD) spectra, etc. Although the importance of these techniques increases constantly, the adsorption/desorption data are widely used because they provide information on the behaviour of a solid with regard to a definite adsorbate. The experimental adsorption/desorption isotherms of nitrogen at 77 K are applied as the standard to measure the specific surface area and the distribution of pore sizes which are most important properties of an adsorbent. According to the IUPAC recommendation, the BET equation has been accepted as the conventional method for determining the adsorbent specific surface area [52,529]. This area can also be determined in terms of the point B method [52]. In both methods, adsorption isotherms are measured, assuming the N₂ molecular size to be 0.162 nm². On the other hand, from the adsorption/desorption isotherms of

nitrogen at 77 K, the suitable pore distribution can be calculated by means of the Kelvin equation. The specific surface area evaluation requires only a monolayer part of the adsorption isotherm, but the pore size-distribution is derived from either the multilayer part of isotherm or by mercury porosimetry [130]. The latter method deals with the penetration into larger pores only, and the suitable distribution function does not include micropores. Low pressure adsorption data are very useful for characterisation of the microporous structure of solids and give an excellent basis for evaluating both the micropore-size distribution and the adsorption potential distribution which is a fundamental source of information on adsorbate–adsorbent interactions.

One of the alternative methods for an assessment of the porosity of solids within the mesopore range was proposed at the beginning of the 1990s (see reference [530] and references therein). The method consists of the measurement of temperature programmed desorption of liquids wetting perfectly the porous solid. Experimentally obtained desorption curves that represent the weight loss of the sample against temperature may be converted into curves for volume loss against the pore/core radius using the Kelvin equation. Specific conditions of thermal desorption experiments cause problems insofar as the surface film remaining on the pore walls of after their emptying may be neglected. The method was tested for several inorganic sorbents, e.g. silica gels, aluminium oxides, spils and activated carbons. 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). Pore size distributions, mean pore radii and total pore volumes derived from thermogravimetric (TG) data are very similar to those calculated from adsorption isotherms measured at static conditions especially for low temperature nitrogen adsorption. Parameters that characterise the porosity of the investigated adsorbents are also very similar to the parameters calculated from mercury intrusion data. The temperature programmed desorption method was also tested for organic porous polymers and nuclear membranes which swell in contact with wetting liquids. Pore size distributions derived from these data differ considerably in comparison to PSD calculated from the adsorption isotherms measured under dry conditions at very low temperature. However, the pore dimensions for nuclear membranes derived from the TG data and small angle scattering data are close to each another. It follows from the data that exist in literature that temperature programmed desorption may be a complementary and alternative method for estimation of the porosity of solids in relation to widely used adsorption and mercury intrusion techniques. By means of this approach the pore size distribution, pore volume and specific surface area of adsorbents and catalysts may be obtained.

It should be emphasised that production of new adsorbents and catalysts and also ion-exchangers is connected with the computational material science that may be considered as a strategic technology for the 21st century [162,164,445].

Computer simulation at the molecular scale of the interaction between the atoms in the frameworks of porous materials and molecules within the pores has come of age and is available using commercial software packages [531–535]. This key approach to the tailoring/design of new microporous adsorbents and catalysts

is used extensively by international chemical and oil companies, and by major industrial gases companies as well. Progress has been made in a number of important areas:

- modelling of known and hypothetical structures to determine their stability, and lowest energy conformations, and, hence, their predicted X-ray diffraction patterns and other spectroscopic properties; this field is well advanced and allows the prediction of stable hypothetical structures and aids in the identification of unknown ones;
- modelling of structure directing molecules for the synthesis of new molecular sieves; the search for specific templates for the synthesis of particular species is analogous to the design of new drugs and therefore uses its appropriate experience;
- modelling of adsorption and diffusion in microporous materials, in particular, Monte Carlo simulations for identification of preferred adsorption sites and for calculation of heats of adsorption; real time molecular dynamics calculations to gain information on diffusion coefficients for systems containing with multiple adsorbate molecules, e.g. at ‘zero’ adsorbate concentration; these procedures begin to allow for a design of microporous materials with adsorption sites for specific molecules (or for species postulated to be the intermediates in catalytic reactions), and of adsorption or catalytic systems with diffusional constraints;
- modelling of reaction pathways is less well developed and requires the extension of quantum mechanical calculations for representative fragments of zeolite frameworks in interaction with the reactants and products of catalytic reactions; major advances can be expected in this field with the development of improved interaction force potentials, electronic basis sets, and computing power, but already a good insight has been gained into the nature of catalytically active Brønsted and Lewis acid sites in zeolites and related metasilicates; and
- modelling of rate processes (concentration vs. time curves) in the cases of complex sorption uptake processes and of multi-component kinetics to properly interpret the rate-limiting mechanisms and to obtain the matrices of rate constants, especially for multicomponent mixtures.

Computer modelling work can directly be connected with the design of improved adsorbents for PSA, VSA, TSA processes (see Section 6) of the various types to tackle a series of separation and purification processes and has to be connected closely with the synthesis work itself.

Thus, there are two main reasons that account for the aforementioned statement regarding the computational material science as the perspective and modern technology for the 21st century [445]: (1) theoretical methods make it possible to calculate a great number of material properties prior to their synthesis; and (2) the performance of computer hardware increases exponentially while its cost diminishes. Computer modelling of adsorbents, catalysts and ion-exchangers will thus become more accurate, faster, more reliable and cheaper compared with experiment. Since an analysis of the number of known compounds shows that the

majority of combination of elements have yet to be made, computational approaches will be a strategic tool to discover the innovative and marked materials. In fact, new developments in this field are the key for development of other areas of science and technology.

6. Practical application of adsorption

As far as applied adsorption science is concerned, in the early ancient times of adsorption history the carbon materials as charcoals were mostly used by some rare specialist. The pioneering use is known of, e.g. Hippocrates who recommended dusting wounds with powdered charcoal to remove their unpleasant odour. However, the rational use of adsorption for industrial purposes started at the end of the 18th century only. The Swedish chemist Carl Wilhelm Scheele, an apothecary by profession, was the first to discover the phenomenon of adsorption of gases on charcoal in 1773 [55]. Twelve years later the Lowitz [57] found that charcoal when immersed in tartaric acid solution, decolourises the later by adsorbing organic contaminants present. This discovery led to the first industrial application of charcoal in the sugar industry in England in 1794, where it was used as a decolourising agent for sugar syrup. This event initiated the research on liquid phase adsorption. The discovery of selectivity of adsorption processes by the Tswett [75] in 1903 originated a new analytical technique, viz. adsorption chromatography. Tswett recommended this process for separation of various mixtures [75].

In 1901 von Ostreyko [87] set the basis for the commercial development of activated carbons through processes that involve the incorporation of metallic chlorides into carbonaceous materials before their carbonisation, and the mild oxidation of charred materials into carbon dioxide or steam at increased temperatures. Based on Ostreyko's patents, in 1909 in Raciborz — on the then German territory — a plant, called *Chemische Werke* was built to manufacture, for the first time on a commercial scale, a powdered, active carbon called eponit. In 1911 a new type of active carbon, known as norit and purit was obtained from peat by its activation with steam and produced in this plant. About the same time as the Raciborz factory was founded, a wood distillation plant was built in Hajnowka (East Poland), initially for manufacturing active carbon solely from wood. In 1911, the NORIT factory in Amsterdam was founded, being now one of the most advanced international manufacturers of active carbons. The process of chemical activation of sawdust with zinc chloride was carried out for the first time in the Austrian plant at Ausing in 1914, and also in the dye plant of Bayer in 1915. At that time, powdered carbons were used mainly for decolourising solutions in chemical and food industries.

World War I introduced the problem of protecting human respiratory tracts from toxic warfare agent introduced intentionally into air. In April 1915 in France, and in May of the same year in the neighbourhood of Warsaw, the German army used warfare gases for the first time against the British and French in the West, and against Russian soldiers in the East. This gave rise to a hasty search for means

of protection. Zelinsky, at the University of Moscow [88] was the first to suggest the use of active carbon as protective medium in gas masks. Such masks, of course with many modifications, are the basis for protecting the respiratory tracts of soldiers throughout the world to the present day. During World War I, coconut shells provided the raw material for the manufacture of active carbon. These world war experiences and research conducted in the 1930s led to the development of new technologies for obtaining granulated active carbons of supersorbon and benzosorbon types. These carbons have found commercial application in the adsorption of gases and vapours. The possibility of purifying municipal gas by removing benzene over active carbon, and other recuperative methods in which this adsorbent was used, has expanded to commercial, widespread utilisation of active carbon [450].

With the development of societies and chemical industry the paramount importance of adsorption phenomena steadily has been recognised [536–539]. Pioneering textbooks were written by Freundlich [92], Adam [540], Schwab [541], Rideal [542] and McBain [93]. Less known is another pioneering book, i.e. by Ledoux [543], which represents the first attempt towards what might be called ‘adsorption knowledge and technology’ because it was aimed to cover many practical aspects of adsorption science, at that time. However, what could be done, even if on a highly empirical level in the 1940s, is no more possible in our times when the adsorption science is very widespread, both in theoretical as well as in practical aspects. *Today, it is impossible to publish a book like that of Ledoux, and even a series of monographs could hardly cover all aspects of applied adsorption science* (e.g. [1–4,40–44,82,84,88,142,159,544–548]). The immensely extended knowledge relevant to multi-fold applications such as in the fields of laboratory, research, industry, agriculture, engineering, materials science, environmental protection is nowadays dispersed in tens of thousand of articles, patents, non-published reports and the like.

Therefore, it is not intended here to present a comprehensive treatment of applications of adsorption, but rather to highlight some important areas, directions and examples and provide reference sources for readers to get to know a problem and for further detailed studies.

6.1. Industrial applications

The fundamental practical applications of adsorption and related areas are following:

- separation and purification of liquid and gas mixtures, bulk chemicals, isomers and air;
- drying gases and liquids before loading them into industrial systems;
- removal of impurities from liquid and gas media;
- recovery of chemicals from industrial and vent gases; and
- water purification.

The commercial adsorption processes for separating gas and liquid mixtures are

accomplished due to selective adsorption of certain substances from their mixtures. The same idea is true for purification of gas and liquid mixtures and drying of some industrial gases. For those purposes, the pore system of adsorbents used is sufficiently wide to enable fast diffusion; separation is caused mainly by selective adsorption that depends upon the van der Waals forces between the adsorbent and the constituents of the gas or liquid mixtures. The above processes are major unit operations in the chemical and petrochemical industries [549,550].

Adsorptive separation and purification are also realised in terms of both steric and kinetic mechanisms. Both of them are usually treated as equilibrium separation processes [4].

A steric separation mechanism is characteristic of microporous adsorbents such as zeolites which have uniform sizes of windows in the crystallographic lattice structure. In their case only small and appropriately shaped molecules can diffuse into the adsorbent space, whereas other molecules are totally excluded. The two largest applications of steric separation deal with drying of the steam from cracking processes over 3A zeolite and the sorbex processes [551]. One most important process that can also be practised by sorbex technology is the separation of *n*-paraffins from iso-paraffins and cyclic hydrocarbons using 5A zeolite [552]. Areas in which further examples on steric separation mechanism are applied relate to drying of natural gases, liquid paraffins, solvents as well as carbon dioxide removal from natural gases [4].

The kinetic mechanism is based on differences in transport rates of different molecules within the pore system of an adsorbent. Such separation is typical of carbon molecular sieves owing to their non-uniform pores size distribution that enables different molecules to diffuse at different rates. This type of separation is commercially used, among others, for nitrogen separation from air [553]. Pressure swing adsorption (PSA) technology is commercially applied for the separation of air as an alternative to the conventional cryogenic processes. Zeolite-based processes, in which the adsorbent shows preferential adsorption of nitrogen over oxygen under equilibrium conditions, is used for the production of oxygen [554–557]. On the other hand, the separation of air for the production of nitrogen is carried out by PSA technology over a carbon molecular sieve [552]. The major typical industrial gas adsorption separations are displayed in Table 6.

One can consider the aforementioned adsorptive processes as alternatives to cryogenic means. By cryogenic separation of gas mixtures is meant the liquefaction followed by distillation. A detailed comparison between utilisation of distillation and adsorption separations processes for the chemical and petrochemical industries has been undertaken by Keller [3]. One can conclude that — in spite of some advantages connected with distillation as simplicity, scalability, capital investment and ability to yield high-purity products — in many cases adsorption processes are more justified, especially when high-purity products are not required. The main reason is associated with the overall costs, which are generally lower for adsorption separation than for distillation. This stems particularly from low energy costs typical of adsorption processes. Moreover, in order to compensate for high energy expenses of traditional distillation processes, this operation is purposefully com-

Table 6
Representative commercial gas-adsorption separations (after Keller [3])

Separation ^a	Adsorbent
I. Gas bulk separations	
Normal paraffins/iso-paraffins, aromatics, olefins	Zeolites
N ₂ /O ₂	Zeolites
O ₂ /N ₂	Carbon molecular sieve
CO, CH ₄ , CO ₂ , N ₂ , NH ₃ /H ₂	Zeolites, activated carbons
Acetone/vent streams	Activated carbon
C ₂ H ₄ /vent streams	Activated carbon
II. Gas purification	
H ₂ O/olefin-containing cracked gas, natural gas, air, synthesis gas, etc.	Silica, alumina, zeolite
CO ₂ /C ₂ H ₄ , natural gas, etc.	Zeolite
Organics/vent streams	Activated carbon, others
Sulfur compounds/natural gas, hydrogen, liquefied petroleum gas (LPG), etc.	Zeolite
Solvents/air	Activated carbon, zeolites
Odors/air	Activated carbon
NO _x /N ₂	Zeolites, carbons
SO ₂ /vent streams	Zeolites, carbons
Hg/chlor-alkali cell gas effluent, other off gases	Zeolites, carbons

^aAdsorbates are listed first.

combined with other separation techniques and utilised, thus, as a hybrid process. For example, for the separation of olefin/paraffin mixtures the following processes have been proposed [558]: extractive distillation, chemical and physical adsorption and membrane separation.

Adsorption appears as one of the most attractive techniques, if particularly practised in accordance with the PSA concept. The economic assessment indicates that alternative hybrid methods of distillation — adsorption are competitive if compared to the traditional process and can represent energy savings between 30 and 50% if they were introduced for separating the propylene — propane mixtures in the actual refineries [559].

Until the late 1950s, the widespread, industrial utilisation of adsorption phenomena remained limited to the purification of air and industrial vent gases [4] beside water treatment and other liquid phase sorption processes. The revolutionary progress in the field has been made, owing to two major events: the invention of synthetic zeolites and the development of new process cycles applied to product recovery and adsorbent regeneration. Any adsorption separation process requires two essential steps: (a) adsorption during which one or more components are preferentially adsorbed/separated; and (b) regeneration during which these components are removed from the adsorbent bed. The adsorbent is repeatedly used in cycles by carrying out steps (a) and (b), either consecutively or in parallel (multi-bed

arrangement). The regeneration of adsorbent permits its reuse in further cycles and enables recovery of the adsorbed substance.

When a regeneration step is carried out through reduction of the total pressure, the process is called pressure swing adsorption (PSA). This efficient technique introduced by Skarstrom [560] and by Guerin de Montgareuil and Domine [561] has become a subject of strong interest in separation and drying processes because of its low energy requirement and development of appropriate sorbents. In the temperature or thermal swing adsorption technology (TSA), the adsorbent is regenerated by heating. When the adsorption step is carried out at near-ambient pressure level and the lowest desorption pressure is sub-ambient, the process is called vacuum swing adsorption (VSA). When the adsorption step is carried out at a super-atmospheric pressure level and the lowest desorption pressure is sub-atmospheric, we can distinguish pressure vacuum swing adsorption (PVSA).

Presently, the PSA/TSA technologies are carried out in terms of various refined and sophisticated variants [547,561–563] that improved the separation and ensured the economy of energy. Separation of mixtures with close boiling points by means of cryogenic methods, such as the propane/propylene and n/iso-paraffins mixtures is very energy consuming [564]. Molecular sieve adsorption technology is the modern answer to separation in order to save energy. Recently, the study of cyclic adsorption processes as PSA/VSA and TSA for the separation of the aforementioned mixtures has been presented by Rodriguez et al. [551].

An important tool in the methodology of gas adsorption process design is the measurement of adsorption isotherms. These isotherms have to be interpreted in terms of suitable theoretical models. Thus, *a significant momentum toward industrial applications of adsorption has been made owing to the elaboration fundamentals underlying the separation processes*. It is noteworthy to mention here the ideal adsorbed solution theory (IAST) introduced by Myers and Prausnitz [291]. As noted earlier, this theory was followed by several theoretical approaches to the equilibrium adsorption of gas mixtures in terms of individual gas isotherms [4,159]. This point is of importance since experimental techniques for the measurement of multicomponent sorption data are generally very time-consuming and difficult to interpret. In the past decade, molecular modelling of PSA/TSA and related cyclic processes has also emerged as an efficient tool for improving our understanding of basic microscopic phenomena and for helping to solve industrial relevant problems ([393,395,549,550] and references therein).

Another important application of adsorption processes is solvent recovery, both from industrial and vent gases. The solvent properties and volatility of organic compounds make them suitable for a great many industrial processes, such as manufacture of paints, polymers, rayon, adhesives and explosives, the extraction of oils from seeds and dry cleaning. However, the high volatility of many spent solvents creates unacceptable problems if they were emitted into the atmosphere, as they constitute health, fire and explosive hazards. These problems can be resolved by collecting the vapour and recovering the solvents for recycling. Adsorbents — mainly activated carbons and highly siliceous zeolites — are usually used in the above mentioned processes. The solvent is recouped by desorption in the

regeneration stage by passing low-pressure steam through the bed in the direction opposite to that of the air flow [565].

Apart from PSA and similar technologies, other important adsorption-related separation methods comprise the following:

- membrane processes ([516,517,566–571] and references therein);
- chromatographic techniques applied in the process scale ([77–84,569,572] and references therein); and
- ion-exchange methods ([569,573–577] and references therein).

All those separation methods play a very important role both in industry and environmental protection.

Heterogeneous catalysis connected closely with adsorption plays a significant role in modern industry and environmental protection [165]. Its numerous applications were discussed briefly earlier. Ion exchange is an important part of the effective removal of impurities including heavy metals and radioactive wastes from liquid media. On the laboratory and industrial scales quantitative separation and qualitative determination of numerous substances are carried out by various chromatographic methods.

In broad terms, most number of scientific problems is associated with adsorption of charged species at solid–liquid interfaces. This gives rise to the formation of electrical double layers that have a topical use in the environment of the soil systems [578,579]. Also, the corrosion inhibition is connected with formation of double layers [580]. These layers play another important role in adsorption analysis [581] and electroanalysis [582]. Adsorption of various solutes by dispersed colloids in liquid solutions can alter the charge of the solids, their dispersion stability, solubility and adhesion on solid surfaces. These changes can be manipulated by the choice of solutes in contact with a given solid and then employed in numerous applications, including catalysis, medical diagnostics, cosmetics, inks, agricultural products, pigment preparations, corrosion, etc. ([571,583–585] and references therein). There is an abundant number of systems between those containing a macroscopic solid–liquid interface and those colloidal in nature. Dyes, soaps or detergents are adsorbed from solution by surfaces of fibres in dyeing and washing processes. Coal cleaning, mineral extraction and soil science are the fields where the adsorption process and solid–liquid interface are of paramount importance [5,6,44,569]. Adsorption is one route to surface modification of solids to design new, reliable, highly-specified adsorbents, selective catalysts, polymer extenders, thickeners of dispersive media and efficient chromatographic packings [524]. Surface modification comprises a main element in flotation, a process in the field of ore refinement [586]. Adsorption can have a dramatic impact on crystal growth, in particular, if some crystal planes are blocked by trace amounts of impurities. In this way, their selective adsorption determines specific growth rates and, thus, the eventual crystal shape [587]. Another area of great practical importance deals with the adsorption of surfactants [586,588]. This process has wide applications in

detergency, flotation, numerous pharmaceutical purposes, cosmetics, paints and the stabilisation of suspensions in general [589].

Recently, extensive studies were performed on the self-assembled monolayers (SAMs) formed by spontaneous adsorption of long-chain, terminally functionalised molecules on various solid films. These molecules form stable monolayers on solids. The long-chains are oriented away from the surface and are present at interfaces with air or liquid. The interfacial properties of SAMs depend on the nature of the terminal functional groups. The SAMs are stable in air and under solvents for months, but they can be destroyed under extreme conditions. At present, SAMs have wide applications in numerous problem solutions [590].

Adsorption of proteins from aqueous solutions at various interfaces represents one of the abundant natural properties of those substances, and investigations are underway of the physicochemical principles of adsorption phenomena that are important to biology, modern technology and environmental protection. Adsorption of proteins has been used in food production for a long time. New applications of adsorbed proteins boost successful development of biotechnology, pharmacology and medicine, determining the usefulness of novel drugs and the control of drug administrations. Regulation of selective adsorption by solid surfaces mixtures of proteins is a major problem of biocompatibility of synthetic materials for medical purposes. Applications of immobilised or adsorbed enzymes as specific catalysts open new routes in modern applied chemistry [591,592].

Only a fraction of the role played by adsorption has been touched upon here. Discussing even a part of adsorption applications and that connected directly or indirectly with related domains goes beyond the limits of this article. The reader can find examples of numerous and well documented applications of adsorption phenomena in industry and in environmental protection in monographs published recently [544,545]. However, to maintain compact and overall character of this review other examples that deal with the importance and role of adsorption processes in many fields of modern industry, technique and everyday life should also be mentioned.

Adsorption processes are used for very thorough purification of monomers — the initial substances for preparation of multimolecular materials. Owing to such purification, polymers of new and desirable exploitation properties are obtained.

Adsorption processes are very important in purification of various petroleum products: fuels, oils, extraction benzenes, etc. Profound drying of natural gas by means of adsorbents prevents from formation of congestion in the gas piping, particularly in regions of low temperatures. Owing to the adsorption process there can be achieved the most effective drying of air before its low-temperature distillative separation into nitrogen, liquid oxygen and noble gases. New high-capacity zeolitic adsorbents are used at large scale for pre-purification of air steams prior to their low-temperature distillation, e.g. [593]. In the same way, dry atmosphere in the technology of semiconductors production is obtained. Adsorbents make it possible to create protective atmospheres during welding and thermal treatment of some important elements of machinery construction. Effectiveness of catalytic processes in the chemical industry depends on the extent to

which initial gases are dried and purified for the contact synthesis which can also be achieved using adsorbents. Their application makes it possible to capture vapours of precious solvents from the atmosphere, to turn them into production, thus decreasing the environmental pollution to large a extent. Adsorbents are widely applied in chemical, food and pharmaceutical industries. Numerous adsorbents are used in the rubber industry as fillers for rubber mixtures, often with vulcanisation accelerating agents which improves the quality of rubber products and removes the defect caused by too early vulcanisation whose sign are listed. Adsorbents are also used for conservation of machinery because they protect from corrosion of metal parts.

Hydrocarbons which are raw materials used for the chemical treatment and in biological processes of valuable protein preparation can be removed from petroleum where heavy paraffins are separated from aromatic and cyclic hydrocarbons and their isomers.

Adsorbents play a significant role in neutralisation of waste gases and sewages and at the same time in capturing valuable components found in wastes. Compared with other methods, adsorbents allow for the most thorough purification of raw materials with relatively low costs. On the other hand, recognition of the mechanism of gas desulfurisation by zeolitic adsorbents — as widely used — and its implications are of outstanding importance to the environment [594].

Adsorbents are widely applied in medicine, among others, to take up poisons found in living organisms and in case of some diseases of the alimentary canal. Lately, adsorbents have been used for purification of blood from noxious substances using chemisorption.

In the pharmaceutical industry adsorbents are used for purification of anaesthetics, removal and purification of vitamins, antibiotics and others. Nowadays, more than half of all pharmaceuticals comprise enantiomers. Often they cannot be often obtained by stereoselective synthesis. The only solution to thus problem is the utilisation of so-called chiral adsorbents to perform separation. This development, however, is still at its beginning.

Of particular importance in laboratory practice are adsorbents used in chromatography for analysis and separation of mixtures with simultaneous evolution of high purity components. Adsorption gas chromatography is used in industrial laboratories for periodical inspection of technological processes and in systems of automatic control and steering of many production processes.

Using adsorbents it is possible to obtain, create and maintain high vacuum, among others, in large size machinery and to ensure long and stable work of semiconducting, cooling and other equipment. Adsorbents make it possible for a man to work in closed spaces, among others, in spacecrafts. Adsorption can also be expected to play a significant role in the environmental control and life support systems on planetary bases, where sorbents may be used to process habitat air or to recover useful substances from the local environment. Another potential application comprises utilisation of adsorbents in automotive exhaust gas purification but also in novel engines to be powered by alternative fuels.

Catalysts, on which approximately 90% processes in chemical plants are based, are as common as adsorbents. Catalysts are applied to produce fertilisers, fuels, polymers as well as modelling pastes, paints and varnishes, synthetic fibres and washing products. At present catalysts and adsorbents are used in almost all fields of science and technology. As mentioned before, adsorption and catalysis are interrelated because most adsorbents are applied in both adsorption and catalytic processes. In the latter case adsorbents either play a function of catalyst supports or are catalysts themselves. Solution of many theoretical and practical tasks depends on the choice of adsorbents and catalysts of optimal surface and porous structure. As follows from the above, it is essential to work out rules of formation and control of porous structure of adsorbents, catalysts and supports of catalytically active substances as beforehand determined properties and to elaborate the methods for their preparation. Preparation of novel adsorbents and catalyst supports with designed porous structure and chemical composition of the surface is one of the most important problems common in adsorption technique and catalysis. The particular determination of structural characteristics of adsorbents and catalysts is based largely on adsorption methods.

6.2. Gas-phase application examples

6.2.1. Drying of gases and liquids by activated alumina

Abundant commercial processes have been developed for dehydration of gaseous mixtures that contain traces of water and for the removal of trace-to-bulk amounts of water from liquid mixtures by the use of activated aluminas as adsorbents. As an example, a PSA technique is shown in Fig. 1 for removal of traces of water from gases by using activated alumina as the adsorbent [595].

The basic concept of a PSA drying process consists of (a) selective adsorption of trace or dilute water from the contaminated gas at a relatively high total gas pressure (50–100 psig) by passing the gas through a packed bed of alumina particles while withdrawing a dry product gas stream until the water concentration at the column effluent rises to a predetermined level and then (b) desorption of the adsorbed water from the alumina by lowering the superincumbent partial pressure of water in the column. Again, the adsorbent is repeatedly used cyclically by carrying out steps (a) and (b). The desorption in PSA process is achieved by (a) lowering the total gas pressure of the column to near ambient and by (b) passing a portion of dry product gas over the column at near ambient pressure. Adsorption at a relatively low pressure (5–10 psig) and desorption under vacuum are also possible options.

Fig. 1 presents a schematic flow diagram for a two column Skarstrom type PSA drier. The process can be used to obtain very dry product gas. The product purity depends on the type of alumina used, feed gas pressure and dry purge gas quantity. Typically a practical PSA drier uses 15–30% of product gas as purge [595]. The typical total cycle time for a PSA process is 2–4 min.

Drying of gases and liquids by activated alumina is a very flexible and versatile process concept. A large variety of synthetic alumina structures that have a range

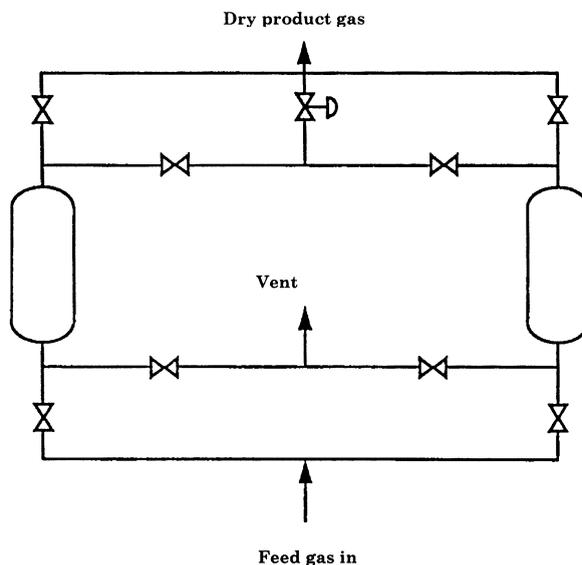


Fig. 1. Schematic flow diagram for two column Skarstrom pressure swing adsorption cycle for gas drying (after Sircar et al. [595]).

of properties for adsorption of water from various gases and liquids, is commercially available [596]. A number of PSA/TSA and other process concepts have been designed to remove trace or bulk water from gaseous or liquid streams [547,562].

6.2.2. Production of nitrogen from air by means of carbon molecular sieves

Nowadays, carbon molecular sieves (CMS) adsorbents find wide industrial applications in gas mixture separations, gas purification processes and as catalysts and catalysts supports. As mentioned earlier, the gas mixture separation processes are based on the specific pore size distribution of CMS, which permits diffusion of different gases at different rates. These processes aim to either recover and recycle valuable constituents from industrial waste gases or to separate small gas molecules by preferential adsorption. At present the latter is at present the most important large-scale application of CMS. Separations that have been accomplished include that of oxygen from nitrogen in air, carbon dioxide from methane in natural gas, ethylene from ethane, linear from branched hydrocarbons as *n*-butane from isobutane, and hydrogen from flue gases.

Production of low cost, high purity nitrogen (99.9%) from air is primarily based on the PSA technique which exploits the micropore structure of CMS to achieve nitrogen/oxygen separation. The PSA process utilises the difference in loading of an adsorptive substance on CMS at high pressure during adsorption, and at low pressure during desorption. The available loading is related either to the equilibrium adsorption or to differences in diffusion rates of the gases. In the case of

oxygen/nitrogen separation, over CMS the kinetic separation mechanism is applicable due to the higher uptake rate of O_2 compared to that of N_2 molecules by the CMS particles. Hence, in the PSA air separation process, the high pressure product is N_2 while O_2 is produced as the low pressure product stream.

A typical PSA system consists generally of two beds filled with CMS as shown in Fig. 2, each being subjected to a series of four distinct process steps, in a cyclic mode. In the first step, high pressure feed gas is introduced into one adsorption bed while concurrently nitrogen gas is produced. The other bed undergoes desorption and regeneration, by venting to the atmosphere or by vacuum. In the next step of pressure equalisation the two beds are brought to an intermediate pressure, by fluid communication. In the third and fourth steps, the first and second steps are repeated with the two beds having changed their roles [597].

The main advantages of the PSA process are the relatively low and maintenance costs, the automatic operation, the easy handling of devices during start-up and energy shut-down procedures, the system flexibility in the change of cycle time, the high purity of products and the long lifetime of vessels. PSA units for nitrogen generation are now used in various applications such as the production of inert gas for the chemical industry and off-shore ships, metal head treatment processes, tank or vessel purging or inertising, food storage, pressure transfer bottling of wine, beer, and other beverages, etc. [598,599].

6.3. Liquid-phase application examples

6.3.1. Adsorption of proteins at solid–liquid interface

Adsorption of proteins at solid–liquid interface is connected — among others — with the problem of biocompatibility of materials. Modern medicine uses exten-

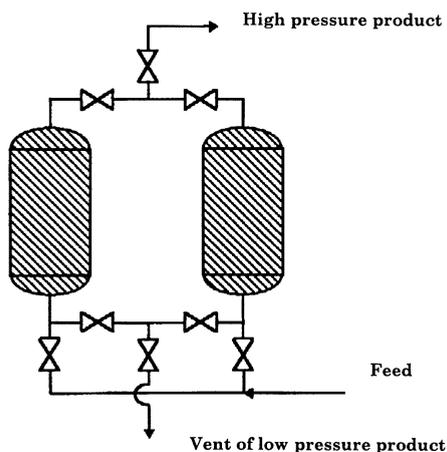


Fig. 2. Typical PSA system for production of nitrogen from air (after Samaras et al. [597]).

sively synthetic materials, polymers and ceramics, in substitution surgery, when surgical intervention requires to replace various organs, vessels, bones and tissues by synthetic ones. This human activity brings to light the problem of biocompatibility, and blood compatibility is its particular case [591]. Current knowledge shows that the problem is connected with the extent of surface energy decrease due to the contact of materials with aqueous media [600]. Biocompatible materials equilibrated with liquid phase have to possess an optimum surface energy of approximately several mJ/m^2 , which allows for prevention of adsorption on the surface of a potentially compatible material of proteins, which promotes intensively the adhesion of platelets resulting into thrombosis. At the same time, the surface energy value cannot be prevented to disperse spontaneously and, thus, to destruct of a material [601]. This task must be investigated using blood-material contacting systems. But such studies are difficult to perform and to control. The problem is solved by now executing blood protein adsorption on synthetic materials. Preferential adsorption of some proteins, for example, serum albumins, results into higher reliability in blood-compatibility of potentially suitable materials *in vivo*. On the contrary, preferential adsorption of fibrinogen and other protein factors of blood coagulation decrease the serviceability of those materials. Thus, adsorption of proteins at biomedical surfaces, such as implants, catheters and insulin pumps, is the first step in a complex series of biophysical/biochemical processes, which determine the biological response to a foreign material.

Interactions of contact lenses with tear proteins are the simplest example of biocompatibility importance. Thus, peculiarities of lysozyme adsorption on the surface of contact lenses can determine both quality and applicability of contact lenses.

The adsorption of three lipids, namely, cholesterol, cephalin and sphingosine from their individual solutions on polycarbonate surfaces and their interaction with proteins and vitamin C has been studied by contact angle measurements and use of labelled proteins. Lipids adsorbed at the surface interact with proteins and platelets. Contact angles and surface energies of polycarbonates exposed to buffer are given

Table 7

Modification of the polycarbonate surface due to cholesterol, protein or cholesterol–protein adsorption (after Izmailova and Yamploskaya [591])

Surface	$\sigma_{\text{bl}}^{\text{a}}$ (mJ/m^2)	θ°	Platelet adhesion
No modification	6.42	70.0 ± 2.0	6.9 ± 1.5
Cholesterol adsorption	20.66	77.0 ± 2.0	10.8 ± 2.0
Cholesterol-albumin adsorption	11.86	62.0 ± 2.5	4.0 ± 1.5
Cholesterol-fibrinogen adsorption	18.22	73.0 ± 1.5	14.0 ± 2.5
Albumin adsorption	10.58	59.5 ± 2.5	3.0 ± 1.0
Fibrinogen adsorption	17.91	72.5 ± 2.0	14.5 ± 1.5

^a σ_{bl} is the surface energy of polycarbonate equilibrated with buffer; θ° is the contact angle of water drop at the surface of the polycarbonate.

in Table 7. The data allow to evaluate the extent to which the polycarbonate surface is modified due to lipid or lipid–protein adsorption.

Table 7 shows that the surface of polycarbonates with adsorbed serum albumin is the most suitable one to be used in implant devices. The behaviour of all lipids toward blood–polymer interaction is by no means similar and may change depending on the nature of the particular lipid, the net charge of the lipid adsorbing surface and the lipid–protein/lipid–platelet interaction at the interface. Under conditions of high cholesterol concentrations the addition of vitamin C leads to suitable surface characteristics of polycarbonates. Malmsten and Lassen [602] have investigated competitive adsorption at hydrophobic surfaces from binary protein solutions. Methylated silica or silica modified by plasma deposition of hexamethyldisiloxane were used as hydrophobic adsorbents. Methods of *in situ* ellipsometry and FTIR were used to measure the protein adsorption.

Preferential adsorption of immunoglobulins (IgGs) and fibrinogen from mixtures with human serum albumin (HSA) was established. However, in sequential adsorption experiments, where HSA was first allowed to adsorb, followed by rising and addition of either IgG or fibrinogen, the additional adsorption is quite limited, and the adsorbed HSA cannot be removed by either IgG or fibrinogen, to any larger extent.

6.3.2. *Water treatment*

Some of the most widespread uses of activated carbons for liquid-phase adsorption are those in water treatment. Recent years have seen remarkable increase in the level of synthetic organic chemicals (SOC) in public water supplies. Hundreds of SOCs such as pesticides, herbicides, detergents, polycyclic aromatic hydrocarbons, nitrosamines, phenolic compounds, trihalomethanes and other pollutants, have been identified in drinking water supplies. On the other hand, natural organic material (NOM) is found in varying concentrations in all natural water sources. It is a complex mixture of compounds formed as a result of decomposition of animal and plant materials in the environment. Most NOM comprise of a range of compounds, from small hydrophobic acids, proteins and amino-acids to larger humic and fulvic acids. The reactions between NOM and disinfectants such as chlorine can form disinfectant by-products, e.g. the reaction of chlorine with humic acids in groundwaters can lead to chlorophenols and halomethanes, and these are indeed the most common products of chlorination. Many of these organic chemicals are carcinogenic. Several methods have been used with varying degrees of success to control contamination of water by organic pollutants. However, the use of activated carbons is perhaps the best broad-spectrum technology available at present. As a consequence, the use of activated carbons in water treatment has increased throughout the world. Granular activated carbon (GAC) adsorption is an effective treatment technology for the removal of organics from drinking water and for improving its taste and odour. In addition, it allows for the removal of trace (heavy) metals such as Cd, Cr, Hg, Cu, Fe, V, Zn and Ni from the water. Activated carbons are being used now on much larger a scale than ever before. Important properties of GAC for water treatment are their adsorptive capacity and selectivity,

stability and ability to withstand thermal regeneration and resistance to attrition losses during transport and handling.

The use of GAC for treatment of municipal and industrial waste waters has developed rapidly in the last three decades. Moving beds, downflow fixed beds and upflow expanded beds have all been used for industrial waste water applications. In most waste water applications, the original cost of carbon adsorbents precludes usually its use on a throw-away basis. Thus, thermal reactivation of hard-coal-based carbons has been proven to be most efficient. Chemical regeneration is generally limited to applications where partial recovery of capacity is acceptable and regenerant disposal is not a problem.

6.4. *Environmental applications*

Every aspect of human activity is closely connected with the natural environment. Whether or not we are aware or care each of us interacts with and affects our environment every day. The rapid development of technology, especially at the end of the 20th century, has increased tremendously the man's ability to produce goods which, in turn, have enhanced his standard of living. On the other hand, this development has also generated a secondary phenomenon, the environment pollution. Such effect led to deterioration of life quality. Thus, improvement of life quality due to innovative technologies has caused negative effects to the environment.

To keep a balance between technology development and the main components of the human environment, appropriate technologies should be used which appear to be a powerful driving force to improve the environment [603]. The relevant activities for upgrading the quality of ground water, drinking water, soil and air have to be developed. Environmental changes affect also the human health and the maintenance of the earth's fauna and flora. Only a few chemical compounds present in the close human surrounding may be considered as beneficial to health. The majority of them act harmfully on humans, even in minimal doses. They occur in all of our environmental media — air, water and soil — and that is why we are obliged to increase all efforts devoted to the human environmental protection. Some of the most important factors in this field are the possibilities and results of modern chemical analyses of pollutants in biological fluids, to maintain human health [604].

Water is one of the most important components of our environment. Nowadays, drinking water is becoming more and more scarce, but our demand for water is becoming greater and greater. A very important problem refers to rising levels of nutrients such as nitrates and phosphates in surface water [605]. Their presence has caused a serious deterioration in water quality of many rivers, lakes and other reservoirs. Therefore, attention has to be paid to the removal of nutrients that originate from sewages and fertilisers, by adsorption methods [606,607], ion-exchange [608] and relevant biotechnological techniques. Phosphorus and its compounds dissolved in ground waters are responsible for the eutrophication in closed water systems, especially in lakes and highly enclosed bays where water is stagnant

[609]. Slag media, wasted by-products from steel industries, are effective adsorbents for phosphorus and its compounds [610].

The earth atmosphere along with water, is the main component of our environment. One essential cause of pollution of the air is the tendency to decrease the cost of manufacturing goods by the use of contaminated raw materials without purifying or enriching them before their application. A preliminary desulfurisation of coal is still rare. When air is used as a source of oxygen, nitrogen in the air is a diluent which, after oxygen consumption, is discharged into the atmosphere together with other impurities. Dusts and smogs are another group of air contaminants. Modern adsorption technologies should restrict emissions of carbon dioxide to prevent increase of the amount of heat dispersed into the atmosphere [607]. This increase, leading to a change of climate, is the 'greenhouse effect'. Another fundamental problem is connected with the removal of volatile organic chloride (VOC) compounds from ground water and recovery of chlorofluorocarbons (CFCs), which are still used in refrigeration and cooling systems. Emission control of ozone depletion by CFCs is very urgent [611].

The pressure on industry to decrease emission of various pollutants into the environment is increasing. A broad range of methods had been developed and is available to control and remove both natural and anthropogenic, municipal, agricultural and other pollutants. With regard to price–performance relation, adsorption technologies comprise most important techniques to overcome the ongoing degradation of environmental quality. They play a significant role both in environmental and human health control as well as in prevention of global warming and ozone layer depletion. The necessity to reduce the concentration of ozone-depleting gases like CFCs and the demand for primary energy diversification in the air conditioning sector, are the main reasons for an increasing interest in adsorption technologies considered as being alternative to, for example the traditional compressor heat pumps in cooling systems [612,613]. Adsorption processes are the 'heart' of several safety energy technologies which can find suitable applications in domestic sectors as reversible adsorption heat pumps, and in industrial sectors as refrigerating systems and heat transformers using industrial waste heat as their primary energy source. They can also be used for technologies to be applied in transportation sectors, for automobile air conditioning or for food preservation in trucks. The adsorption-based desiccant dehumidification technology is also emerging as an alternative to vapour compression systems for cooling and air-conditioning. Desiccant-based systems can improve indoor air quality and remove air pollutants due to their coadsorption by the desiccant materials. Moreover, a number of micro-organisms are removed or killed by the desiccant. Other problems are production of drinking water [614–616], removal of anthropogenic pollutants from air, soil and water [617–620] as well as removal of micro-organisms from the indoor air [621]. They offer important tasks to adsorption technologies. Adsorption can also be expected to play a significant role in the environmental control and life supporting systems or planetary bases, where sorbents may be used to process the habitat air or to recover useful substances from the local environments. Adsorption processes are good candidates for separation and purification in

space by virtue of such characteristics as gravity independence, high reliability, relatively high energy efficiency, design flexibility, technological maturity, and regenerability. For this reason, adsorption has historically played a key role in life support on piloted U.S. and Russian spacecrafts [622]. Another environmental dilemma deals with the removal of SO_x and NO_x from hot combustion gases. The above mentioned problems may be solved by advanced adsorption techniques [623]. Among them, the rapid pressure swing adsorption (PSA) methods are very efficient for solving both global and local environmental issues [605,611]. The term of global environmental problem refers to emission of ozone-depleting gases like CFCs, VOCs and of 'greenhouse' gases (CO_2 , CH_4 , N_2O , etc.). The term local environmental problem refers to flue gas recovery (SO_x and NO_x), solvent vapour fractionation and solvent vapour recovery, waste water treatment and drinking water production.

Other environmental issues regard solid aerosols of industrial origin, which are incomplete combustion products. Their surfaces can adsorb many toxic organic chemicals. Thermal and photochemical reactions of adsorbed and chemisorbed species may result in their transformation into even more toxic forms. Those can be delivered to the human organism with the respirable fraction of aerosols or through drinking water. Thus, solid aerosol surfaces are harmful as precursors to the synthesis of strong toxics, carcinogens and mutagens. Migration of solid aerosols to areas with other types of organic and inorganic pollutants can create unexpected combinations of chemicals in the atmosphere. The investigation of the adsorption and chemical reactions of organic pollutants on industrial-aerosol surfaces present very important environmental challenge [624].

Automobiles contribute substantially to man-made hydrocarbon emissions. A new type of activated carbon filter for the application in Evaporative Loss Central Devices (ELCD) was developed by NORIT [625]. Automobiles had to pass the so-called SHED emission test, that was legislated in Europe in 1992 [625]. A comparable standard test is in force in the US for many years.

Adsorption of metals into living or dead cells has been termed as biosorption. Biosorption that deals the metal–microbe interactions includes both terrestrial and marine environments. Biosorption by sea bacteria plays a significant role in detoxification of heavy metals in aqueous systems. The literature on the influence of biosorption in metal crystal formation is rather scant. The subject of microbe participation in nucleation and halite crystal growth is important with regard to the influence of cell surface layer (S-layer) components on the crystal habit [626].

Only a fraction of issues for which adsorption methods play a paramount role, adsorption methods have been touched here. However, as follows from above considerations, the subject of utility of modern adsorption technologies has enormous environmental, economic and legal impact. It constitutes a serious challenge as far as prospects for further intense development are concerned.

In Table 8 the most important environmental tasks related to adsorption techniques are summarised.

In order to illustrate the environmental utility of adsorption phenomena let us consider two spectacular examples.

Table 8
Typical environmental tasks related to adsorption science

Local environmental problems	
Flue gas treatment	SO _x , NO _x and mercury emissions removal
Solvent recovery and solvent vapour fractionation	Volatile organic compounds (VOCs) recovery from the working environment, among them from ground water; adsorption methods are needed to prevent VOCs emission into air by increasing emphasis on development and use of air purification (AP) and solvent vapour recovery (SVR) processes.
Waste water treatment	Organics, nitrogen and phosphorus removal, i.e. removal and recovery of nutrients from waste water.
Drinking water production	Deterioration of water sources, advanced treatment of waste water, etc.
Dessicant dehumidification technology	Improvement of indoor air quality and removal of air pollutants and the number of microorganisms either removed or killed by dessicants due to coadsorption by dessicant materials.
Global environmental problems	
Global warming control	Emission control of 'greenhouse' gases (CO ₂ , CH ₄ , N ₂ O); utilization of CH ₄ .
Ozone layer depletion	Recovery of CFCs in emission control of ozone-depleting gases, still used in refrigeration systems.

Table 8 (Continued)

Global environmental problems	
Defense applications	Removal of contaminants used in defense tasks, that present extreme toxic chemical agents; experience gained during the Gulf War have awareness of the need in better air purification (AP) systems designed especially for defense applications; in contrast to the solvent vapour recovery (SVR) processes, defense systems have only to purify air, but both applications are environmentally related where adsorption technology is used quite successfully.

6.4.1. Adsorption heat pumps

In the field of heating and cooling, research activity is mainly addressed towards finding alternative solutions to vapour-compression heat pumps, since these machines use valuable electricity energy as primary energy and polluting refrigerants, as CFCs which are dangerous both for ozone depletion and the ‘greenhouse’ effect [627]. Amongst new systems recently proposed, adsorption machines provide characteristics that make them a good techno-economic alternative to vapour compression machines. In fact, adsorption machines can utilise environmental friendly refrigerants and efficiently medium–low temperature heat (100–200°C) as primary energy. In addition, they have no moving parts and a simple regulation of energy production in response to load request can be practised [628].

Gas adsorption phenomena are strictly correlated to energy transfer and transformation, and they are regulated by temperature and pressure. Taking into account these properties and combining endothermic desorption with exothermic adsorption processes in closed cycles, it is possible to realise an adsorption heat pump whose external effect is equal to that obtained with vapour-compression machines using an inverse Carnot cycle [629].

It follows from Fig. 3 that adsorption machines are mainly composed of three principal components [630]: the adsorber reactor (R) that contains the solid adsorbent placed in a suitable heat exchanger, the evaporator (E) and the condenser (C). In the adsorber reactor both the desorption and the adsorption processes occur at different times and at different temperature and pressure conditions. An adsorption machine works at four temperature levels, one for each component but in practice, it is designed so that there are three temperature working conditions: high, medium, low (T_h , T_m , T_l).

The thermodynamic cycle for heat pumping is divided into two phases: the

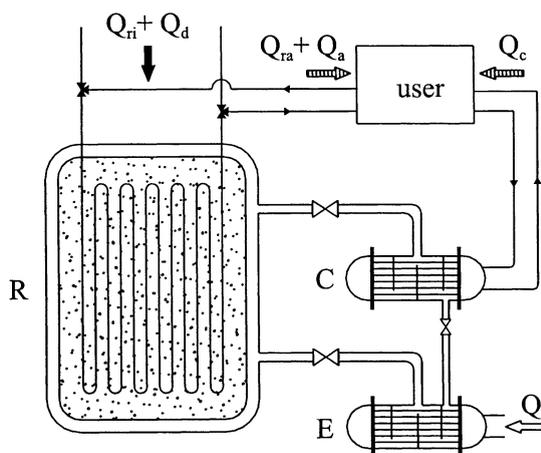


Fig. 3. Scheme of the adsorption machine: C, condenser; E, evaporator; R, adsorber bed (after Cacciola and Restuccia [630]).

charge and the discharge. During the first phase, the solid adsorbent is dried, and the refrigerant fluid here adsorbed evaporates due to the heat furnished to the system at high temperature T_h . The desorbed vapour flows into the condenser (C) where it condenses at medium temperature T_m and, consequently, releases useful heat. At the beginning of this first phase, incoming heat into the adsorber increases both temperature and vapour pressure till the condenser pressure is overcome, then the vapour, previously in equilibrium with the solid, flows towards the condenser due to the small difference in pressure now created between adsorber and condenser. The vapour movement makes the desorption process possible under isobaric conditions. Then, during this charge phase external heat ($Q_{ri} + Q_d$) is furnished to the system at high temperature T_h by means of a thermal vector fluid flowing into the heat exchanger placed inside the solid adsorber (R), and, at the same time, heat Q_c is released from the system at medium temperature T_m , from the condenser.

The discharge phase, which consists of the vapour adsorption process on the solid adsorbent, allows the heat coming from the low temperature T_l to be transferred to the medium temperature source T_m . This phase starts with the cooling of the solid adsorbent and the consequent decreasing of pressure, till it reaches the evaporator vapour pressure. The evaporator (E) is maintained at the low temperature T_l due to an external fluid that transfers heat coming from the low temperature source.

As during the charge phase, the small difference in pressure between evaporator and adsorber creates the non-equilibrium conditions that allow the refrigerant vapour to flow from evaporator to the solid adsorbent bed where it is adsorbed. During the cooling of the solid and afterwards the adsorption process, thermal energy ($Q_{ra} + Q_a$) is produced and externally transferred immediately through the heat exchanger placed into the solid adsorbent. In this way, the evaporator produces continuously vapour which is adsorbed isobarically in the solid bed. This phase represents the useful effect of the system, in fact, heat is taken away from a low temperature and released to a medium temperature source, realising, in this way, a heat pump or cooling effect, similar to that obtainable with an inverse Carnot cycle.

6.4.2. *Adsorption devices in spacecraft environmental control*

The environmental control and life support system on a spacecraft maintains a safe and comfortable environment in which the crew can live and work by supplying oxygen and water and by removing carbon dioxide, water vapour, and trace contaminants from cabin air. Among a variety of operations aimed at the recycling of air and water, the adsorption processes are very promising [631]. These include separation and reduction of carbon dioxide, removal of trace gas-phase contaminants, recovery and purification of humidity condensate, purification and polishing of waste water streams, and others. Several of these recycling processes can be performed totally or in part by adsorption equipment.

The design ultimately selected for use on international space station (ISS) is represented schematically in Fig. 4 [631]. It includes an activated charcoal bed, a

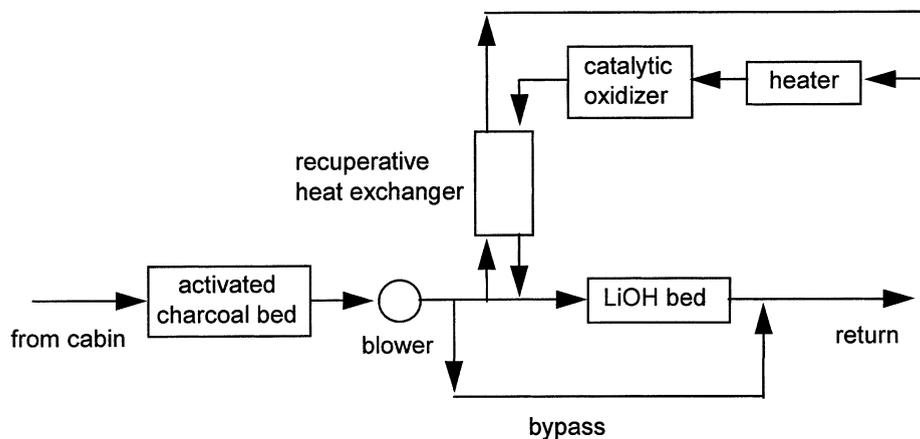


Fig. 4. ISS trace contaminant control subsystem scheme. The activated charcoal bed removes high molecular weight organics and potential catalysts poisons. The catalytic oxidizer destroys low molecular weight compounds that are not captured by the charcoal bed. The LiOH bed removes acid produced by oxidation of halocarbons (after DallBauman and Finn [631]).

catalytic oxidiser, and a LiOH bed. The charcoal bed removes high molecular weight compounds that cannot be readily desorbed and is therefore an expendable item. It also removes ammonia, which is a potential catalyst poison. The bed contains 22.7 kg charcoal impregnated with 10 wt.% phosphoric acid to enhance its ammonia removal capability. Cabin air flows through the bed at 15.5 m³/h. After leaving the bed, the process stream is split so that 4.6 m³/h is routed through a catalytic oxidiser where low molecular weight compounds are destroyed and then through a post-sorbent bed containing LiOH to remove acid gases produced in the oxidiser [632]. The remainder of the air bypasses the oxidiser and LiOH bed.

7. Environmental analysis

Environmental analysis is a discrete and sophisticated branch of analytical chemistry in which different analytical techniques are applied: adsorption/chromatographic, adsorption/electrochemical, spectroscopic and spectrophotometric methods are of great importance. Environmental analysis is in fact mostly applied trace analysis, if pollutants are present in trace and ultra-trace quantities. Thus, environmental analysis requires a fast, modern and reliable methodology to detect pollutants in very small quantities within a short time and with a high degree of precision [633]. Let us consider two examples of environmental analysis relevant to adsorption science.

7.1. Electrochemical analysis of adsorbable surface active substances (SAS)

This type of analysis deals with the formation of electrode/double-layer due to

the adsorption of many chemical compounds — both organic and inorganic — at the solution/electrode interface. This process effects the properties of the electrode/double-layer in a measurable manner, and it forms the basis for electrochemical analysis of adsorbable SAS present in the solution. Historically first should be mentioned the polarographic adsorption analysis introduced by Heyrovsky [634] and the tensammetry developed from polarography or measurement of differential capacity of the electrode double layer [635]. From practical point of view — with respect to recent voltammetry methods — it is necessary to point out procedures based on adsorptive accumulation of the analyte on the electrode surface [636]:

- adsorptive stripping voltammetry; and
- adsorptive stripping potentiometry.

The scope of applications of the above methods ranges from metal trace analysis, to analysis of organic compounds and in general to environmental, biochemical, pharmaceutical, toxicological and other applications [637].

7.2. *Chromatographic methods preceded by sampling and sample preparations*

Adsorption phenomena are widely applied for the sampling of air, surface water and waste water [638]. The sampling is realised together with enrichment of analytes. Owing to selectivity of adsorption, pollutants of interest are selectively removed from the bulk sample matrix, preconcentrated, cleaned-up, separated into individual substances and analysed by gas and liquid adsorption chromatography, or related chromatographic techniques (HPLC, TLC, etc.) [639].

Among the adsorption methods applied for isolating analytes from liquid matrices and for their preconcentration, practical importance has the solid phase extraction (SPE) technique. The idea of SPE consists in retention of analytes from a large sample volume on a small bed of adsorbent, and following elution of analytes, with a small volume of solvent. The selection of appropriate parameters of adsorbents and solvents is the base condition for successful employment of this method [640].

8. Trends and perspectives

The future development of adsorption science represents a major challenge to industry and environmental fields because it is of low cost, and provides regenerability of most of the adsorbents used and potential ability to design and manufacture novel materials specific for a given need. On the other hand, *the perspective of adsorption will be shaped by the rigorous relationship between theory, experiment and practice. This means that special attention has to be given to the evolution of new theories stimulated by results of conventional experiments, modern instrumentation techniques and by 'experimental data' obtained from computer simulations.*

The following extended comments can be made with regard to forthcoming of adsorption science:

1. New applications of adsorption methods will emerge, as new types of adsorbents specific for a given need will be developed. The fruitful advantage of new micro- and mesoporous adsorbents like MCMs materials or of nanostructured solids will be tremendous if their production, cost and other practical constraints will be managed and controlled appropriately. In this context, the dramatic progress in instrumentation that allows for detailed characterisation of adsorbent materials including microporous solids seems to be very important. Invention and revelation of novel adsorbents, catalysts and related materials with specific applications is a major feature of contemporary materials chemistry.
2. Commercial applications of adsorption phenomena have to be developed in juncture with new underlying theoretical approaches and molecular simulations of industrial processes. The same holds for adsorption techniques, in particular that those include new class of adsorbents, catalysts, membranes and ion-exchangers.
3. Another field in continuous progress is that of expansion of new separation techniques for bioadsorption purposes. In this context, the improvement and further development of chromatographic techniques demonstrates huge practical importance. A similar challenge also exists for various types of membrane separation methods that present very advanced and innovative molecular separation units with great potential for applications in all sectors of industry. A number of bioseparation goals can be approached by hybrid processes that combine the processes of adsorption, filtration, chromatography, etc. These hybrid adsorption processes if utilised for separation and purification of macromolecules such as polysaccharides, lipids, proteins, nucleic acids and other biological molecules, are very promising for bioadsorption purposes. Further extensive investigation on this subject is anticipated.
4. Areas in which further developments are expected, deal with the equilibrium and transport phenomena of fluids in porous materials, with special emphasis on diffusion. In this regard, one of the important element will require the maintenance of a suitable balance between theoretical and experimental research. One would expect, however, that a wide range of sophisticated modelling and simulation methods will level the enormous gap between microscopic and macroscopic picture scales.
5. The prospective demands toward adsorption and related domains are based on a growing concern for environmental control and for increase of life quality. Many of the aspects aimed to this concept will require both the use of new adsorbents, catalysts or like materials and the development of the ecology-friendly, low-energy adsorption technologies. In this context, the PSA, TSA and other separation and purification techniques will prove to be more favourable in terms of simulation and experiment research.

We can observe a perspicacious progress in all of these subjects, and thereby adsorption has a bright future.

9. Summary and conclusions

Adsorption science has a very long history, and its first practical adoptions were noted in ancient times. The current adsorption theory and relevant applications initiated by Langmuir's fundamental work have been developed extensively during the last 80 years. Presently, they comprise very advanced approaches that include a wide spectrum of modern surface chemistry. The autonomous existence of adsorption science is due to two unquestionable facts:

- the enormous complexity that is inherent to adsorption phenomena at various interfaces, and
- the widespread, general occurrence and importance of adsorption and related domains in nature, including everyday life's products, industrial and environmental applications.

The present status of adsorption has been illustrated by a wide range of theoretical descriptions as well as by several practical examples, including industrial and environmental tasks. The crucial role of molecular modelling to understand adsorption phenomena and to develop novel classes of adsorbent materials has proven to be extremely valuable if used in conjunction with experimental techniques. This tendency will certainly continue and computer modelling will increasingly yield results identical with those from experiments. *It must be stressed that new theoretical approaches and new groups of adsorbents generate new practical applications.* This evolution creates a whole set of challenges and issues towards adsorption and related domains including catalysis, membrane separation, ion-exchange and process scale chromatography. Aforementioned branches deal with appropriate technologies that reduce the ecological load, introduce renewable energy sources, allow for strategies for selection and search for ecology-friendly processes as well as formulation of criteria for estimation of acceptability of current chemical technologies and for design and production of new revolutionary solid materials.

It is widely known, that broadly-understood adsorption science has gained a dominating role in modern industry under environmental, economical and energy saving aspects. Doubtless, adsorption technologies are rapidly improved and adopted to contemporary tasks of mankind. Both industrial as well as recent environmental problems require wide body scientists and engineers to develop the theory of adsorption science and to produce new adsorbents, catalysts and other advanced solids of great practical importance. Nowadays, only such technologies which give the possibility of sustainable development of people and society are justified. Adsorption, catalysis and aforementioned related fields have a major impact on development in many areas central to the question of our future. In this

context they may be esteemed as technologies of the 21st century. To summarise: *quod erat demonstrandum* — which was the thing to be proved.

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