ANNALES
UNIVERSITATIS MARIAE CURIE-SKŁODOWSKA
LUBLIN – POLONIA
VOL. LVI, SECTIO AA 2001

Adsorption contribution to the protection of the human environment

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Our concern in this paper is to review those current trends in adsorption science that address the question of protection of human health and environment. The subject matter is preceded by fundamental information on adsorption, basic types of adsorbents and some general information on practical tasks of phenomenon under consideration. 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 examples.

1. INTRODUCTION

Adsorption of one or more components at a given interface takes place when the concentration of this component at the interface, i.e., at the so-called surface phase, is different from that in the bulk neighbouring phases. The phenomenon of adsorption results from the existence of an anisotropic force field, which affects the molecules placed at the given interface. The process under consideration can occur at the following systems: liquid-gas, liquid-liquid, solid-liquid and liquid-liquid.

The major development of adsorption processes on a large, industrial scale deals mainly with the solid-gas [1] and solid-liquid [2] interfaces, but in various laboratory separation techniques all types of interfaces are applied [3]. The fundamental conception 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.

Another basic conception in adsorption occurring at every interface is the real adsorption system. Let us consider this conception 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 connected 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.

Adsorption can result either from the van der Waals universal interactions (physical adsorption, physisorption) or it can have a character of the chemical process (chemical adsorption or chemisorption). Contrary to physisorption, the chemisorption only occurs as a monolayer [3]. Physical adsorption can be compared to the condensation process of the adsorptive.

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 IUPAC [4].

2. GENERAL CONSIDERATIONS

Certain phenomena, which we now associate with adsorption were known in ancient times, but the first quantitative observations were carried out by Scheele [5] in 1773 and Fontana [6] in 1777 who reported some experiments of the uptake of gases by charcoal and clays.

Modern application of adsorption is connected with Lowitz's observation [7] who used charcoal for decolourization of the tartaric acid solution as a result of organic impurities uptake. Systematic studies of adsorption dating from the works by de Saussure [8] started in 1814.

Papers by Chappuis [9], Joulian [10] and Kayser [11] have the great importance among of papers of the 19th century. Their achievements are included in Table 1.

McBain [12] in 1909 introduced the term "absorption" 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 these two phenomena and to define them precisely. In doubtful cases, the term "sorption" and consequently the terms "sorbent", "sorbate" and "sorptive" are used.

Practical application of adsorption processes is based mainly on selective uptake of individual components from their mixtures with other substances. Selective adsorption was discovered by the Russian scientist Tswett in 1903 [13].

For convenience the main points dealing with the early experimental period of adsorption are shown in Table 1.

The isotherms dealing with physical adsorption of gases and vapours give most important characteristics of industrial sorbents which include, among others, pore volume, pore size or energy distribution and surface area. These very specific curves can be interpreted in order to obtain information about the adsorption mechanism strictly connected with interactions between adsorbent and adsorbate molecules and give the possibility to assess the efficiency of industrial adsorbents applied in separation, purification and other utilitarian processes.

Tab. 1. The most important facts on the early experimental period of adsorption

Date	Explorer	Significance
1	2	3
3750 BC	Egyptians and Sumerians	Use of charcoal for the reduction of copper, zinc and tin ores in the manufacture of bronze
1550 BC	Egyptians	Application of charcoal for medicinal purposes to adsorb odorous vapours from putrefactive wounds and from intestine
460 BC	Hippocrates and Pliny	Applied charcoal to treat a wide range of affections including epilepsy, chlorosis and anthrax
460 BC	Phoenicians	The first recorded application of charcoal filtres for purification of drinking water
157 AD	Claudius Galen	Applied carbons of both vegatable 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 [5]

1	2	3
1786, 1788	Lowitz	Used charcoal for decolourization of the tartaric acid solution as a result of organic impurities uptake [7]
1793	Kehl	Discussed the application of charcoal for the removal of odours from gangrenous ulcers and applied the carbons of animal origin for removing colours from sugar [14]
1794		The charcoal was used in the sugar industry in England as a decolourization agent of sugar syrups
1814	de Saussure	Started the 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 [8]
1881	Kayser	Introduced into literature the terms: "adsorption", "isotherm" or "isotherm curve"; also developed some theoretical concepts which became a basis for a monomolecular adsorption theory [9]
1881, 1889	Chappuis	Made the first colorimetric measurements of heat during wetting of various types of carbon by liquids [9]
1901	von Ostreyko	Set the basis for the commercial development of activated carbons through the processes involving 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 [15]
1903	Tswett	Discovered the phenomenon of selective adsorption during separation of chlorophy and other plant pigments by means of silica materials. Introduced the term: "column solid-liquid adsorption chromatography". This discovery was not only the beginning of a new analytical technique, but also started a new field of surface science [13]
1904	Dewar	Found the selective adsorption of oxygen from its mixture with nitrogen during the air uptake by charcoal [16]
1909	McBain	Proposed the term "absorption" to determine a much slower uptake of hydrogen by carbon than adsorption. Also proposed term "sorption" for adsorption and absorption [12]

1	2	3
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
1914 – 1918		World War I created the problem of protecting man's 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 the gas mask [17]
1941	Martin and Synge	Introduced laboratory practice the solid-liquid partition chromatography, both in column and planar form [18]
1955	Barrer and Breck	Invented the method of zeolite synthesis. In this year the North-American Linde Company started production of synthetic zeolites on a commercial scale [19]

It should be clearly emphasized that the correct interpretation of experimental adsorption isotherms can be realized 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 adsorption system. The model assumptions usually are the result of the experiment observation. The experimental results allow the formation of 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 of the suitable adsorption equation. Thus, a theory is tested in order to explain the behavior of the adsorption system investigated. A theory always serves as a guide to new experiment and is constantly tested. Adsorption science has been developed by a constant interplay between theory and experiment.

In Table 2 the paramount facts dealing with early theoretical period of adsorption are shown.

Catalysis plays an extremely important role in modern industry, environmental protection and our everyday life. Moreover, its importance in sustainable development is beyond discussion. Approximately, it accounts for as much as 90% of chemicals and materials manufactured throughout the world. Catalysis, as a vital process, is technology of the 21st century. The term catalyst denotes a body or a material, which accelerates a chemical reaction but does not appear in the chemical equation of this reaction. It enhances the rate of the reaction, and finally it is regenerated at the end of it. Usually, catalysts are classified both as homogeneous and heterogeneous ones. Homogeneous catalyst occurs in the same phase as the reactant, but heterogeneous catalyst is in a different phase. Heterogeneous catalysis includes heterogeneous catalysts, which are typically solids. Besides, the important subdisciplines of the process under consideration are biological, enzymatic and photo-catalysis [29].

Catalysis, contrary to chromatography is not derived directly from the science about adsorption. But it cannot be considered apart from adsorption, particularly from adsorption at the solid-gas and solid-solution interfaces. As it is generally known, most adsorbents play a role of catalysts or their supports. In consequence, methods of preparation and characterization of adsorbents as well as 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 [29].

Adsorption and catalysis are closely related to each other. The following remarks are right:

- action of solid catalysts results from their capability of reacting substances adsorption,
- the same porous solids can be used as adsorbents, catalysts supports and catalysts,
- chemical character and size of solid surface areas, their porous structure, mechanical properties and thermal stability play an essential role in adsorption and catalysis,
- development of theoretical studies on adsorption, design and production of new adsorbents affect heterogeneous catalysis evolution.

The development and application of adsorption cannot be considered separately from the development of technology 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.

Tab. 2. The most important facts of the early theoretical period of adsorption

Date	Name	Significance
1	2	3
1888	Bemmelen Boedocker Freundlich	The so-called Freundlich empirical equation was first proposed by van Bemmelen. It is known in literature as Freundlich equation, because Freundlich assigned great importance to it and popularized its use [20]

1	2	3
1911	Zsigmondy	Discovered the phenomenon of capillary condensation [21]. This phenomenon is described by means of Kelvin equation for cylindrical pores, with the pore width in the range 2 – 50 nm
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 of the temperature [22]
1918	Langmuir	Derived for the first time a clear concept of the monolayer adsorption, formed on energetically homogeneous solid surfaces (kinetic studies). The statement proposed by Langmuir applied to chemisorption and with some restrictions, to physisorption [23] It ought to be stressed at this point that the Langmuir studies of the adsorption of gases by surfaces, led to the formulation of a general treatment of the kinetic reactions and surfaces
1932	Langmuir awarded the Nobel Prize	Langmuir realized that the surface catalysis is usually preceded by chemisorption and he interpreted the kinetics of surface reaction in terms of his monolayer equation. In 1932 Langmuir was awarded the Nobel Prize in chemistry for his discoveries and researches in the realm of surface chemistry [24]
1938	BET	The milestone towards the development of the adsorption science was the multilayer isotherm equation proposed by Brunauer, Emmett and Teller in 1938 [25]. This theory was preceded by two significant works by Brunauer and Emmett in 1935 [26] and 1937 [27] who for the first time were successful to determine – 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 four-adjustable parameter equation, where the forces of capillary condensation were taken into account. This equation as the complex, was seldom used in the literature
1946	Dubinin-Radushkevich	Proposed the theory of the volume filling of micropores (TVFM) [28] This approach originated from the potential theory of adsorption introduced by Eucken and Polanyi [22]

In our early history, active carbon was the first in widely used as an adsorbent. Its application in the form of carbonized wood (charcoal) has been described as early as 3750 BC in an ancient Egyptian papirus. 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, characterization and applications were published [30] and the interested readers are advised to consult the suitable literature. The same holds true in the case of other adsorbents of great practical importance (Table 3).

The development of the adsorption technique was based on various types of adsorbents: before World War I on carbon adsorbents, in the period between World War I and World War II on active carbons, silic acid gels and aluminium oxides. After World War II revolutionary progress was made owing to discovery and application of synthetic zeolites [31]. At present, besides 40 natural zeolites, there are known over 150 synthetic ones.

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 regarding novel porous materials, both inorganic and carbonaceous ones.

Tab. 3. Main types of adsorbents of great practical importance

Carbon adsorbents	Mineral adsorbents
Active carbons	Silica gels
Activated carbon fibres	Activated alumina
Molecular carbon sieves	Oxides of metals
Mesocarbon microbeads	Hydroxides of metals
Fullerenes	Zeolites
Heterofullerenes	Clay minerals
Carbonaceous nanomaterials	Pillared clays
	Inorganic nanometarials

The most representative porous solids are activated carbons [32] and zeolites [33]. Recently, the research achievements on this subject are well represented by the pore size engineering that by changing raw materials and preparation conditions it is possible to create structurally different forms of the same porous solid. In terms of pore size engineering one can obtain a wide class of nanoporous materials which have different pore geometry and chemical nature. Nanoporous solids are very popular in science and technology due to their application in various separation, purification and environmental processes [34].

Discovery of molecular carbon structures as fullerenes, heterofullerenes [35] and carbon nanotubes [36] has provided a new impetus to search for new selective adsorption applications of such materials. Carbon nanotubes represent a new generation of nanoporous solids with great potential for selective adsorption and shape selective separation. The interest is to computer design of their effective molecular sizes for the bulk separation of hydrocarbon molecules of industrial importance. The selective adsorption of molecules over ceramics and extraction with supercritical fluids is also an emerging technology.

A comprehensive review related to adsorption on new and modified inorganic sorbents was presented recently in the monograph [37]. It should be emphasized that production of new adsorbents and catalysts and also ion-exchangers is connected with the computational material science, which may be considered as a strategic technology for the 21st century.

Practical applications 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 in order to remove their unpleasant odour. However, the rational use of adsorption for industrial purposes started at the end of the 18th century. The Swedish chemist Carl Wilhelm Scheele was the first to discover the phenomenon of adsorption of gases on charcoal in 1773 [5]. A dozen years later the Russian academician Lowitz [7] found that charcoal when immersed in the tartaric acid solution, decolorizes it by adsorbing the organic contaminants. This discovery led to the first industrial application of charcoal in the sugar industry in England in 1794, where it was used as a decolorizating agent for sugar syrup. This event initiated the research on adsorption from the liquid phase. The discovery of adsorption process selectivity by the Russian scientist Tswett [13] in 1903 originated a new analytical technique, which is adsorption chromatography. Tswett recommended this process for separation of various mixtures.

During World War I there arose the problem of protecting man's respiratory tracts from toxic warfare agent introduced intentionally into the air. This gave rise to a hasty search for means of protection. Zelinsky [17] was the first to suggest the use of active carbon as the adsorption medium in gas masks. Such masks, of course with many modifications, are the basis for protecting the respiratory tracts of soldiers throughout the world up to the present day. During World War I, coconut shells provided the raw material for production of active carbon. These world war experiences and researches conducted in 1930's led to the development of new technologies for obtaining granulated active carbons of supersorbon and of benzosorbon types. These carbons have found commercial application in the adsorption of gases and vapours. The possibility of purifying municipal gas by removing benzene using active carbon, and other recuperative methods in which this adsorbent was used, have extended to commercial, wide-spread utilization of active carbon.

Nowadays, the fundamental practical applications of adsorption are the following:

- separation and purification of liquid and gas mixtures,
- drying gases and liquids before loading them into the industrial system,
- removal of impurities from the liquid and gas media,
- recovery of chemicals from industrial and vent gases.

The commercial adsorption processes for separating gas and liquid mixtures are accomplished due to selective adsorption of certain substances from their mixtures. This same idea is true of purification gas and liquid mixtures and drying some industrial gases. In this separation mechanism, the pore system of adsorbents used is sufficiently wide to enable fast diffusion; separation is caused by selective adsorption, which depends upon the van der Waals forces between adsorbent substrate and gas or liquid mixtures.

The examples of numerous applications of adsorption phenomena in industry and in environmental protection are included in the recently published monographs [38-39]. However, one should also mention other examples showing the importance and role of adsorption processes in many fields of modern industry, technique and everyday life.

Adsorbents play a significant role in neutralization 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. Adsorption processes are very important in purification of various petroleum products: fuels, oils, extraction naphtas etc. A large number of adsorbents are used in the rubber industry as fillers for rubber mixtures, often with vulcanization accelerating agents which improves the quality of rubber products.

In the pharmaceutical industry adsorbents are used for purification of anaesthetics, removal and purification of vitamins, antibiotics and others. Today more than fifty per cents of the pharmaceuticals are enantiomers. They cannot be often obtained by means of stereoselective synthesis. Then, the only solution of the problem is to apply the so-called chiral adsorbents to perform separation. 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.

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

Adsorbents make it possible to work in closed spaces, among the others, in spaceships. 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.

Adsorption contribution to the environmental protection. Every aspect of human activity is closely connected with the natural environment. Whether or not we are aware, or care, every day each of us interacts with and affects our environment. The rapid development of technology, especially at the end of the 20^{th} century, has increased enormously man's ability to produce goods, which 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, the improvement of the life quality owing to innovative technologies caused negative effects for the environment.

In order to keep the balance between technology development and main components of the man's environment the appropriate technologies should be used, which appear to be a powerful force for the improvement of the environment [40]. The relevant activities for upgrading the quality of ground water, drinking water, soil and air have to be developed. The environmental changes affect also the human health. Only few chemical compounds present in the human close surrounding may be considered beneficial for health. The majority of them act harmfully on humans, even in minimal doses. They occur in our environmental media-air, water and soil and that is why we observe the increasing efforts devoted to the human environmental protection. One 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 [41].

Water is one of the most important components of our environment. Nowadays, the drinking water is becoming more and more scarce, but our demand for water is becoming greater and greater. A very important problem is concerned with the rising levels of nutrients such as nitrates and phosphates in the surface water [42]. Their presence has caused a serious deterioration in the water quality of many rivers, lakes and reservoirs. Therefore, the attention has to be given to the removal of nutrients originating from sewages and fertilizers by adsorption methods [43], ion-exchange [44] and relevant biotechnological techniques. Phosphorus and its compounds dissolved in the ground waters are responsible for the eutrophication in the closed water system, especially in lakes and highly enclosed bays where water is stagnant [46]. Slag media, wasted by-products from steel industries, are effective adsorbents for phosphorus and its compounds [47].

The earth atmosphere along with water, is the main component of our environment. One of the essential causes 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 desulfurization of coal is still rare. When air is used as a source of oxygen, nitrogen in the air is a diluent which, after the oxygen consumption, is discharged into the atmosphere together with other impurities. Dusts and smogs are another group of air contaminants. The modern adsorption technologies should restrict emissions of carbon dioxide to prevent increasing the amount of heat being dispersed into the atmosphere [44]. This increase, leading to a change of climate, is the greenhouse effect. The other 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 [48].

The pressure on industry to decrease the emission of various pollutants into the environment is increasing. A broad range of methods is available and developed to control and remove both natural and anthropogenic, municipal, agricultural and other pollutants. In relation to the price/performance, adsorption technologies are the most important techniques to overcome the degradation of the environmental quality. They play a significant role both in environmental and human health control and in prevention from global warming and ozone layer depletion. The neccessity to reduce the ozone depletion gases like CFCs and the demand for primary energy diversification in the air conditioning sector, are the main reasons for the increasing interest in adsorption devices considered alternative to the traditional compressor heat pumps in the cooling systems [49]. Adsorption processes are the "heart" of several safety energy technologies which can find suitable applications in the domestic sectors as reversible adsorption heat pumps, and in the industrial sectors as refrigerating systems and heat trasnformers using industrial waste heat as the primary energy source. They can also be used for technologies to be applied in the transportation sectors, for automobile air conditioning or for food preservation in trucks. The adsorption dessicant dehumidification technology is also emerging as an alternative to vapour compression systems for cooling and conditioning air for a space. Dessicant base systems can improve indoor air quality and remove air pollutants due to their coadsorption by the dessicant materials. Moreover, a number of microorganisms are removed or killed by the dessicant. Other problems are production of drinking water [50-51], removal of anthropogenic pollutants from air, soil and water [52-53] as well as removal of microorganisms from the indoor air [54] and other important tasks to solve in terms of 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 U.S. and Russian piloted spacecrafts [55]. Another environmental dilemma deals with the removal of thermal SO_x and NO_x from hot combustion gases. The above mentioned problems may be solved by advanced adsorption techniques [56]. Among them, the rapid pressure swing adsorption (PSA) methods are very efficient for solving both global and local environmental issues. By the term of global environmental problem is meant emission of ozone depletion gases like CFCs, VOC and emission of green-house gases (CO_2, CH_4, N_2O, etc.). The term local environmental problem deals with flue gas recovery (SO_x and NO_x), solvent vapour fractionation and solvent vapour recovery, wastewater treatment and drinking water production.

Other environmental issues concern the industrial solid aerosols of industrial origin, which are the incomplete combustion products. Their surfaces can adsorb many toxic organic chemicals. Thermal and photochemical reactions of adsorbed and chemisorbed species may result in their transformations into 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, carcinogenes and mutagenes. Migration of solid aerosols to areas with other types of organic and inorganic pollutants can create unexpected combinations of chemicals in the atmosphere. The investigations of the adsorption and chemical reactions of organic pollutants on the industrial aerosol surfaces present very important environmental challenge [57].

Automobiles contribute substantially to man-made hydrocarbon emissions. A new type of activated carbon filtres for the application in Evaporative Loss Central Devices (ELCD) were developed by NORIT. Automobiles had to pass the so-called SHED emission test, which was legislated in Europe in 1992 [58].

Adsorption of metals into living or dead cells has been termed as biosorption. Biosorption dealing with the metal-microbe interactions include both terrestrial and marine environments. Biosorption by the sea bacteria plays a significant role in detoxification of heavy metals in the 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 [59].

Only a fraction of the role played by adsorption methods has been touched upon here. However, as follows from the above considerations, the subject of utility of modern adsorption technologies has enormous environmental, economic and legal importance and constitutes a serious challenge with the prospects for further intense development.

In Table 4 the most important environmental tasks related to adsorption techniques are summarized.

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

Water treatment. One of the most widespread uses of activated carbons for liquid-phase adsorption is in water treatment. Recent years have seen an 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 the breakdown of animal and plant material in the environment. Most NOM consists of a range of compounds, from small hydrophobic acids, proteins and aminoacids to larger humic and fulvic acids. The reactions between NOM and disinfectants such as chlorine can produce disinfectant by-products, e.g. the reaction of chlorine with humic acids in groundwaters can produce chlorophenols and halomethanes. These are indeed the most common products of chlorination. Many of these organic chemicals are carcinogenic. Several methods have been used with varying success for the control of organic pollutants in water. However, the use of activated carbons is perhaps the best broad-spectrum technology available at the present moment. As a consequence, the use of activated carbons in water treatment has increased in the world. Granular activated carbon (GAC) adsorption is an effective treatment technology for the removal of organics from drinking water supplies and for improving taste and odour. It is also a practicable technique for the removal of trace (heavy) metals such as Cd, Cr, Hg, Cu, Fe, V, Zn and Ni. Activated carbons are now being used on a much larger scale than ever before.

Tab. 4. Typical environmental tasks related to adsorption science

A. 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 the ground water; the adsorption methods are needed to prevent VOCs emission into air by increasing emphasis on the development and use of air purification (AP) and solvent vapour recovery (SVR) processes
Wastewater treatment	Organics, nitrogen and phosphorous removal, i.e. removal and recovery of nutrients from wastewater
Drinking water production	Deterioration of water sources, advanced treatment of wastewater, etc.
Dessicant dehumidification technology	Improvement of indoor air quality and removal of air pollutants; the number of microorganisms are removed or killed by the dessicant due to coadsorption by dessicant materials
B. Global environmental problems	
Global warming control	Emission control of green-house gases (CO_2, CH_4, N_2O); utilization of CH_4
Ozone layer depletion	Recovery of CFCs in emission control of ozone depletion gases, which are still used in refrigeration systems
Defense applications	Removal of contaminants used in defence tasks, which present extreme toxic chemical agents; experiences gained during the Gulf War have heightened the awareness of the need for better air purification (AP) systems designed specially for defence applications; in contrast to the solvent vapour recovery (SVR) processes, defense systems only have to purify air, but both applications are environmentally related, where adsorption technology is used quite successfully

Important properties of GAC for water treatment are their adsorptive capacity and selectivity, ability to withstand thermal regeneration and resistance to attrition losses during transport and handling.

The use of GAC for the treatment of municipal and industrial wastewaters has developed rapidly in the last 25 years. Moving beds, downflow fixed beds and upflow expanded beds have all been used in industrial wastewater applications. In most wastewater applications, the cost of virgin carbon usually precludes its use on a throwaway basis, so the thermal reactivation of hard, coal-based carbons has proved to be both economical and practicable. Chemical regeneration is generally limited to applications where partial recovery of capacity is acceptable and regenerant disposal is not a problem.

Adsorption heat pumps. In the field of heating and cooling production, 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 green-house effect [60]. Among the new systems recently proposed, adsorption machines present many characteristics which make them a good techno-economic alternative to vapour compression machines. In fact, adsorption machines can use 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 realised [61].

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 the endothermic desorption with the exothermic adsorption processes in closed cycles it is possible to realise an adsorption heat pump whose external effect is equal to that obtained with a vapour-compression machine using an inverse Carnot cycle.

It follows from Figure 1 that adsorption machines are mainly composed of three principal components [62]: the adsorber reactor (R) with 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, 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 charge and the discharge. During the first phase, the solid adsorbent is dried and the refrigerant fluid here adsorbed evaporates thanks 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 flows towards the condenser thanks 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 temperature T_h by means of a thermal vector fluid flowing into the heat exchanger placed inside the adsorber (R). At the same time, heat Q_c is released from the system at medium temperature T_m from the condenser.

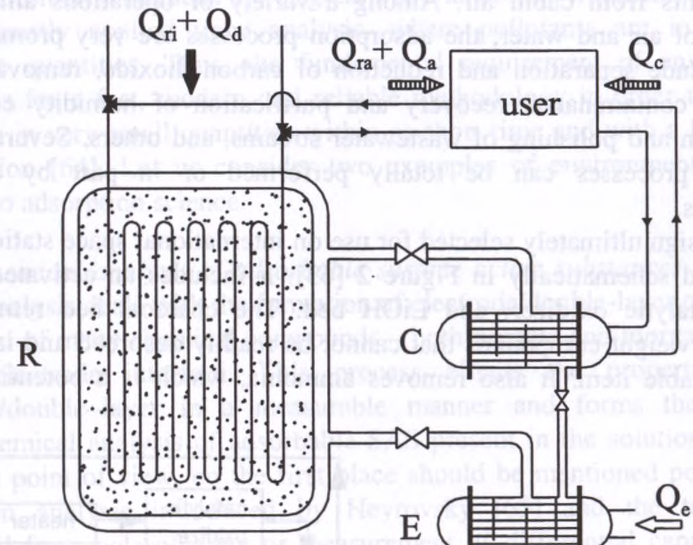

Fig. 1. Scheme of the adsorption machine: C – condenser; E – evaporator; R – adsorber bed (after Cacciola and Restuccia [62])

The discharge phase 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 the pressure, till it reaches the evaporator vapour pressure. The evaporator (E), in fact, is maintained at the low temperature T_l thanks to an external fluid, which 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, which 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 immediately externally transferred through the heat exchanger placed into the solid adsorbent. In this way the evaporator continuously produces vapour which is isobarically adsorbed in the solid bed. Heat (Q_e) 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 obtained with an inverse Carnot cycle.

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 [63]. These include separation and reduction of carbon dioxide, removal of trace gas-phase contaminants, recovery and purification of humidity condensate, purification and polishing of wastewater streams, and others. Several of these recycling processes can be totally performed or in part by adsorption equipments.

The design ultimately selected for use on international space station (ISS) is represented schematically in Figure 2 [63]. It includes an activated charcoal bed, a catalytic oxidizer, and 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.

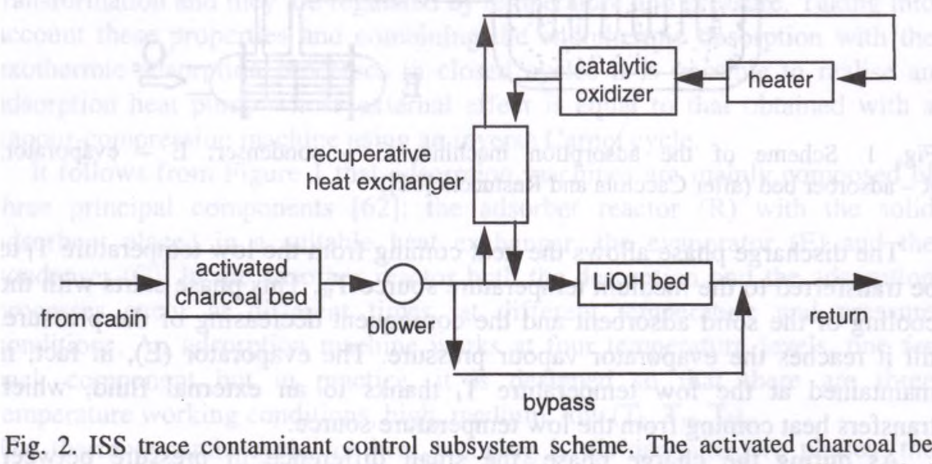

Fig. 2. ISS trace contaminant control subsystem scheme. The activated charcoal bed removes high molecular weight organics and potential catalysts poisons. The catalytic oxidizer destroys low molecular weight compounds that are not captured by the charcoal bed. The LiOH bed removes acid produced by oxidation of halocarbons. (after DallBauman and Finn [63])

The bed contains 22.7 kg charcoal impregnated with 10% weight phosphoric acid to enhance its ammonia removal capability. Cabin air flows through the bed at 15.5 m^3/hr. After leaving the bed, the process stream is split so that 4.6 m^3/hr is routed through a catalytic oxidizer where low molecular weight compounds are destroyed and then through a post-sorbent bed containing LiOH to remove acid gases produced in the oxidizer. The remainder of the air bypasses the oxidizer and LiOH bed.

Environmental analysis. This 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, where pollutants are in trace and ultra-trace quantities. Thus, the fundamental requirement of environmental analysis is for a fast, modern and reliable methodology in order to detect of pollutants in very small quantities within as short time and with a high degree of precision [64]. Let us consider two examples of environmental analysis relevant to adsorption science.

Electrochemical analysis of adsorbable surface active substances (SAS). This kind of analysis deals with the formation of electrode/double-layer owing 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 forms the basis for electrochemical analysis of adsorbable SAS present in the solution. From the historical point of view, on the first place should be mentioned polarographic adsorption analysis introduced by Heyrovsky [65] and the tensammetry developed from polarography or measurement of differential capacity of the electrode double layer. From a 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:

- adsorptive stripping voltammetry,
- 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 [66].

Chromatographic methods proceeded by sampling and sample preparations. Adsorption phenomena are widely applied for the sampling of air, surface water and wastewater [67]. The sampling is realized 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.).

Among the adsorption methods applied for isolating analytes from liquid matrixes 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 ellution 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 [68].

3. 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 works have been developed extensively during the last eighty years and presently comprises very advanced approaches including a wide spectrum of modern surface chemistry. The autonomous existence of adsorption science is due to two unquestionable facts:

- to the enormous complexity which is inherent to the adsorption phenomena at various interfaces, and
- to 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 range of theoretical descriptions as well as by some practical examples, including environmental tasks. 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 concerning adsorption and related domains including catalysis, membrane separation, ion exchange or process scale chromatography. Aforementioned branches deal with technologies for reducing the ecological load, introduction of renewable energy sources, strategies for selection of and search for ecology-friendly processes, 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, the 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 are justified, which give the possibility of sustainable development of the people and society. Adsorption, catalysis and aforementioned affined fields have a major impact in many areas central to the question of our future. In this context they may be esteemed as the technologies of 21st Century.

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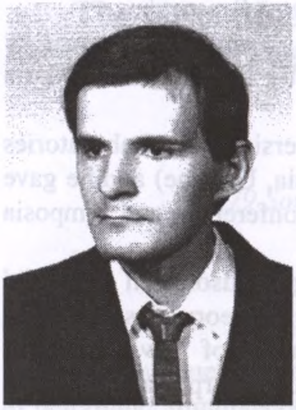
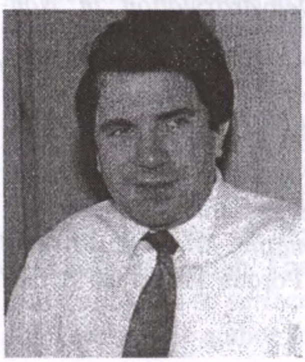
CURRICULA VITAE



Przemysław Podkościelny was born in 1966, Lublin, Poland. Graduated from Maria Curie-Skłodowska University in Lublin. Since 1990 employed in Department of Theoretical Chemistry, Faculty of Chemistry MCS University as an assistant. In 1996 he obtained Ph.D. degree on the basis of dissertation entitled: "The methods of determination of capacity of surface phases formed onto homogeneous and heterogeneous solid surfaces". Main field of interest is theoretical description of adsorption processes, which occur at gas-solid and liquid-solid interfaces, preparation and investigation of new adsorbents, application of fractal theories to adsorption and practical aspects of adsorption.



Andrzej Dąbrowski was born in Poland in 1947. After graduation from the Institute of Chemistry, Maria Curie-Skłodowska University in June 1970, he was employed in the Department of Physical Chemistry as an assistant. In 1976 received his PhD degree and was employed in the Department of Theoretical Chemistry as a lecturer. From April 1986 to March 1992 he held the position of associate professor. On March 1st 1992 he was appointed professor of MCS University. From September 1987 to February 1989 he held the position of Vice-Dean of the Chemistry Faculty. From September 1990 to August 1996 he held the position of Dean of the Chemistry Faculty. On July 1st 1997 obtained the title: professor of chemistry. Member of the: Polish Chemical Society, American Chemical Society, International Adsorption Society and International Association of Colloid and Interface Scientists. Member of IUPAC-Commission on Colloid and Surface Chemistry Including Catalysis for the term 2000-2001. Member of the Committee Chemistry of the Polish Academy of Science.

He was involved in several projects aiming at theoretical description of adsorption processes occurring at gas-solid, liquid-solid interfaces and theoretical studies of gas and liquid chromatographic analysis methods. He published over 120 papers and edited two monographs: *Adsorption on New and Modified Inorganic Sorbents* (Elsevier, 1997), *Adsorption and Its Applications in Industry and Environmental Protection* (Elsevier, 1999). He is the member of Advisory Board of *Industrial & Engineering Chemistry Research*.

For his outstanding scientific achievements, he was awarded five times by the Polish Ministry of Education and twelve times by the Rector of Maria Curie-Skłodowska University.

He has made several scientific visits in many Universities and Laboratories (USA, France, Germany, Japan, China, Hungary, Russia, Ukraine) and he gave also keynote and invited lectures during international conferences and symposia (Belgium, Israel, China, Hungary, Portugal).

Research areas: Theory of single and mixed gas adsorption on solid surfaces, Theory of liquid adsorption on solid surfaces, Theory of solid/liquid adsorption chromatography, Preparation and investigation of new adsorbents for adsorption and chromatography, Practical aspects of adsorption and related domains.

Selected publications:

1. *Monte Carlo Simulation of Silica Surface Dehydroxylation in Non-Isothermal Conditions*, Langmuir, 13, 928 (1997).
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