

ADSORPTION OF GASEOUS POLLUTANTS

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Summary

This chapter introduces the fundamentals of the adsorption of gaseous pollutants, including laws of its equilibrium and kinetics. Various forms of internal diffusion are methodically discussed. The chapter *Adsorbents and Adsorption Processes for Pollution Control* is devoted to the main characteristics of adsorbents and associated processes with special emphasis on technical aspects and general design guidelines in environmental applications, particularly in gas cleaning and separation.

1. Scope

1.1. Definitions

Adsorption is an important unit operation in chemical engineering, even though it is much less used than most of its counterparts. Its major handicap is in requiring an auxiliary solid, the adsorbent, whereas most other operations involve only fluids that are much simpler to circulate. This explains the batch operating mode and cyclic character of numerous adsorption operations.

In a wider sense adsorption can take place on any interface between any set of two phases, on either a fluid-fluid interface (liquid-gas, liquid-liquid), or a solid-fluid interface (solid-gas, solid-liquid). Adsorption usually refers to the increase in concentration of the target compound on the solid surface of a porous material, selected as adsorbent, since the latter found most practical applications.

Adsorption is often confounded with absorption. Adsorption involves a concentration of a chemical at the surface; absorption addresses a concentration in the bulk of the material. Organics dissolve into plastics, hence absorb, rather than adsorb on the surface.

Adsorption is often reserved for cases in which all simpler methods have failed. Since it achieves a high degree of removal of the pollutant (up to 99 % and sometimes even higher), it is often used as a final polishing step, after removing all easier separable pollutants.

Generally a gas flow is treated by adsorption with the particular purpose of removing a trace impurity or only a minor amount of pollutants: since the adsorption capacity of any adsorbent is limited, it is most rational to apply this method only when the concentration of a target compound is low. Adsorption is effective mainly when a contaminant ranges from 1 ppb to 1000 ppm. Such an approach allows increasing considerably the duration of operation of a gas cleaning facility in its adsorption stage, before switching to the stages of regeneration of the adsorbent (desorption, drying and cooling). When large amounts are to be cleaned, other methods are mostly preferred, for the temporal ratio of loading the adsorbent versus its regeneration becomes too unfavorable.

Adsorption is both a phenomenon of partition between phases and a mass transfer

process, in which molecules from the gas phase or from a solution are bound onto a solid surface in a condensed layer (generally).

1.2. Applications

Adsorption is used for separation, cleaning or drying of both liquid and gaseous effluents in such different fields as industry, medicine, environmental protection, etc. Some examples of technical applications are:

- Drying of gases, e.g. to obtain a low moisture content as required for instrumentation or in cryogenic applications (see *cryo-condensation Condensation, Control of Carbon Monoxide and Volatile Organic Compounds*);
- Catalytic processes, where adsorption is one first step of a complex phenomenon leading to chemical conversion. Chemical reaction is facilitated while molecules are adsorbed or more precisely chemisorbed onto a surface. After a molecular rearrangement, the converted molecule should be desorbed and enabled to leave the catalyst;
- Gas/Solid chromatography, an analytical technique, in which compounds are separated by their specific rate of migration through a partition column, filled with suitable adsorbent (see *Effluent Gas Monitoring*);
- Separation of linear and branched or cyclic hydrocarbons, present in oil mixtures;
- Food discoloring, e.g. in sugar production;
- Purification of pharmaceutical products.

There are also many other ways, in which adsorption can be used. Purification of liquid streams is based on the similar principles as that of gases: both proceed in a fixed bed arrangement, but liquids can also be treated by stirring/mixing. In what follows, emphasis is placed strongly on environmental applications, particularly the treatment of off-gases, and much less - on industrial applications, such as:

- Pressure Swing Adsorption, a cyclic process using molecular sieves for separating gases, e.g. air into oxygen and nitrogen;
- Drying of gas streams, on mineral adsorbents, such as alumina, molecular sieves or silica gel;
- Heterogeneous catalysis.

The above processes may also be applied in an environmental context. Some examples of applications in a specific pollution control include:

- Removal of odorous substances from landfill gas;
- Recovery of volatile organic compounds (VOCs) and solvent vapors from air;
- Treatment of industrial off-gases containing products of incomplete combustion (PAHs, dioxins and other halogenated aromatic compounds) as well as CO, SO₂ and CO₂;
- Decrease of NO_x emissions from exhaust of vehicles;

- Cleaning of wastewater from persistent or non-biodegradable pollutants, etc.

Regardless of the specific application, the selection of the most suitable adsorbent and designing the equipment are the main practical issues. A brief overview of technical adsorption units and guidelines for their design are treated more fully in a second article.

1.3. Main Features

For each particular task an adsorbent is selected on the basis of its main features:

- Capacity,
- Selectivity,
- Kinetics,
- Regeneration possibilities,
- Compatibility and
- Cost.

Usually, these characteristics are to be established experimentally, which generally requires extensive testing, since each adsorbent and adsorbate behaves differently. Experimental results are also not to be extrapolated beyond the investigated domains.

Pressure drop over a packed bed is well predictable, from correlations based on the Darcy's or Kozeny-Carman's Law (see *Adsorbents and Adsorption Processes for Pollution Control*). Adsorption as a rule is stronger, when the adsorbate has a lower vapor pressure and a higher molecular weight. The presence of water vapor tends to reduce adsorptive capacity, water molecules competing with the adsorbate for adsorption sites or surface. Polarity and concentration levels also play an important role. In case different compounds are present in the gas phase, adsorption may become a competitive process, so that stronger adsorbing chemicals may replace previously adsorbed molecules. Conversely, weaker adsorbing molecules may also displace strongly adsorbed ones, if the former are very numerous and the residence time is sufficiently long for effecting such replacement.

Selectivity is strongly affected by polarity, vapor pressure, and the nature and structure of the adsorbent. Physical and possibly chemical kinetics is another very important issue since it controls the cycle time of an adsorption bed, markedly influences the shape of the breakthrough curve and hence the effective time available to conduct the operation.

1.4. Transport Phenomena

The target compound travels from the bulk gas to the external surface (external diffusion), then continuing its route inside the particle by a combination of molecular, surface, Knudsen and other types of internal diffusion. Smaller pore diameter leads to higher internal surface, but may retard or impede internal diffusion.

1.5. Regeneration

Regeneration and reuse of adsorbent are technically possible and desired in almost all cases, unless the cost of adsorbent is negligible, as is the case with waste materials, put to use as an adsorbent, or when the operation is close to a quarry of mineral adsorbents. The recovery of adsorbate is also desirable, e.g. of solvents, unless there is no use for the compounds separated, e.g. in case these are smells. The decision whether to employ such recovery and reuse is based on several economic, environmental and technical considerations. However, currently it is becoming uncommon to design a system in which a high-value adsorbent is discarded after one use.

The regeneration can be performed either in-place, or off-site. Much depends on the duration of the adsorption run: this is typically of the order of one day or some fraction thereof when recovering solvents, of several months when using the adsorbent bed as a police filter.

2. Scientific Principles of Adsorption

2.1. Adsorption Forces

A simple picture regarding the nature of physical adsorption relates to the reduction in vapor pressure, exerted by attraction forces between a surface and a condensable vapor.

Physical adsorption is the result of van der Waals interactions between adsorbate(s) and the adsorbent. These forces are weak and characterized by a small change of enthalpy, which is insufficient to lead to bond breaking. Physical adsorption does not involve a sharing or transfer of electrons, so that all interacting species maintain their identity. The interactions between the partial electric charges of polar molecules are responsible for creating attractive contributions to these forces. Repulsive components prevent the complete collapse of matter to nuclear densities.

Chemical adsorption or chemisorption is characterized by the superior strength of the adsorbent – adsorbate bond even approaching that of an ordinary covalent bond, so that the chemical nature of gases or vapors may be significantly different in the adsorbed state (cf. catalysis). There is no sharp distinction, however, between physical or chemical adsorption, rather a somewhat gradual transition scaled by the strength of adsorption. Moreover, there is no material distinction between physical and chemical adsorption in actual applications or in their technical aspects.

The main features of the both types are as follows:

- The spectroscopic, electron spin resonance and magnetic susceptibility measurements are the most reliable way to identify the type or strength of adsorption. They can confirm whether a transfer of electrons occurs and chemical bonds are formed.
- The simplest test criterion for distinguishing chemisorption from physisorption is based on a comparison of the enthalpies of adsorption. The heat of physical

adsorption is normally below 20 kcal/mol (84 kJ/mol), but this value may be exceeded for adsorbents with very narrow pores. The heat of chemical adsorption is approaching that of chemical bonds and varies in a very wide range, starting at less than 40 kcal/mol (168 kJ/mol), to more than 100 kcal/mol (418 kJ/mol). Thus, activation energy is required for chemisorption.

- Physical adsorption is not site-specific; adsorbed molecules are free to cover the entire surface, so that the surface of solid adsorbents can be measured by determining the adsorbent amount (B.E.T.-method: see under Section 2.6). Chemisorption is restricted to specific surface sites so, that chemisorbed molecules are no longer free to migrate about the surface.
- These physical adsorption interactions are fully reversible, whereas chemisorption is irreversible under specific operating conditions. Desorption at the temperature levels required is accompanied by decomposition of adsorbate.

Therefore, chemical sorption has certain advantages over its physical alternative in gas cleaning. However, regeneration of adsorbent becomes more difficult and energy demanding at the same time, and recovery of adsorbate is sometimes impossible, since destructive desorption takes place at the temperature and operating conditions required.

2.2. Pore and Surface Characteristics

Each adsorbent is characterized by its structural properties, including its

- Surface area (external, internal, total and specific),
- Porosity, tortuosity, and pore size distribution.

Surface area plays a fundamental role in the physical adsorption of a specific adsorbent. For understanding the various kinetic issues (see Section 3) it is important to distinguish between external and internal surfaces. The former constitutes only the minor part of the total surface area of an adsorbent and consists from an ideal geometric surface, i.e. that of an equivalent sphere or cylinder and augmented with the surface represented by all those prominences and cracks, which width is greater than their depth. The internal surface is associated with the walls of pores that have narrow openings extending inward from the granule surface to the interior of this granule. Another important parameter for the theory of adsorption is specific surface area (a_s , $\text{m}^2 \text{g}^{-1}$), which is defined as the total surface area divided by the mass of the adsorbent.

According to their size, pores are classified into three groups; each of these has its special functions during adsorption:

- Macropores ($> 0.2 \mu\text{m}$) are relatively large channels allowing internal transport to the sites of adsorption proper;
- Mesopores (1.5 nm - $0.2 \mu\text{m}$) are responsible for further distribution of the adsorbate throughout the porous structure and feature mono- and multilayer adsorption;
- Micropores ($< 1.5 \text{ nm}$) are with dimensions in the range of the size of a molecule. The total volume of micropores in industrial adsorbents usually does

not exceed $0.5 \text{ cm}^3 \text{ g}^{-1}$ and constitute the most of the internal surface. Adsorption takes place according to capillary condensation mechanism.

For the sake of comparison, a dioxin molecule, consisting of three condensed cycles, more precisely two aromatic nuclei internally linked by two ether bonds, has dimensions of the order of 0.7 to 1.4 nm. The surface area values for nil- to octachlorinated dioxins vary from 186 to 315 \AA^2 . The molecular volume of a series of polyaromatic hydrocarbons (PAHs) lies between ca. 128 to 261 \AA^3 ; their surface area ranges from ca. 156 to 282 \AA^2 .

Porosity (ϵ , %) is the percentage of the total volume of the adsorbent that consists of pore space. In other words, it reflects the portion of the free volume. Porosity can be related either to a separate granule or to a layer of the adsorbent. The latter depends on the shape of the granules and the density of packing of the layer.

Tortuosity, τ , (in German: Labyrinthfaktor, Zick-Zack-Faktor) reflects the shape of the pores and affects the rate of molecular diffusion in the particle. It can be defined as a ratio of actual pore length to the superficial diffusion path. Its value has to be determined for each kind of adsorbent to estimate the pore diffusion coefficient. Available methods and models are (see later in this article):

- The pore diffusion model with chromatography method
- The pore diffusion model with the Wicke-Kallenbach method
- The combined diffusion model with the transient response method.

Since tortuosity is a structural parameter, it is independent of temperature and of the nature of the diffusing species.

2.3. Equilibrium Data

The free, non-adsorbed gas and the adsorbed gas (adsorbate) are in a dynamic equilibrium that can be moved by acting upon temperature, total pressure, and composition of the gas phase, in particular the concentration of adsorbate and the presence or absence of vapors competing for adsorption. The amount of adsorbate can be expressed using either surface concentration (in mol m^{-2}), or as surface coverage (θ , in %) defined as ratio of number of adsorption sites occupied to the number of adsorption sites available.

The equilibrium partition between the free and adsorbed state depends on temperature and pressure and can be described in terms of an empirical function $q = f(P, T)$, which can vary as:

$q = f(P)$	Isotherm	$T = \text{const}$	
$q = f(T)$	Isobar	$P = \text{const}$	where q – is the amount adsorbed.
$q = f(T)$	Isostere	Fixed surface coverage	

An adsorption isotherm is the most widely used form for representing equilibrium data,

because it is the most convenient form both to obtain and to plot experimental data. Moreover, this is the form in which theoretical treatments are most easily developed. The most common types of isotherms and related theories are described below.

2.4. Langmuir Theory

2.4.1. Basic Assumptions

Langmuir's theory (1918) is based on the following assumptions:

- The adsorbing surface area consists of a series of sorption sites that are equivalent to each other
- The ability of a particle to bind to a sorption site is independent of whether or not nearby sites are occupied
- Adsorbed molecules form at most a monolayer on the sorption surface. The latter corresponds to a complete coverage.

Each of these assumptions is somewhat open to criticism. The Langmuir theory is most popular in studies of catalysis and widely applied in a number of variations.

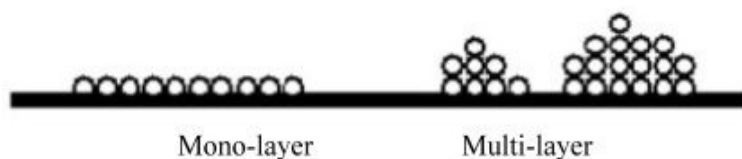


Figure 1: Monolayer and multilayer

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Biographical Sketches

Alfons Buekens was born in Aalst, Belgium; he obtained his M.Sc. (1964) and his Ph.D (1967) at Ghent University (RUG) and received the K.V.I.V.-Award (1965), the Robert De Keyser Award (Belgian Shell Co., 1968), the Körber Foundation Award (1988) and the Coca Cola Foundation Award (1989). Dr. Buekens was full professor at the Vrije Universiteit Brussel (VUB), since 2002 emeritus. He lectured in Ankara, Cochabamba, Delft, Essen, Sofia, Surabaya, and was in 2002 and 2003 Invited Professor at the Tohoku University of Sendai.

Since 1976 he acted as an Environmental Consultant for the European Union, for UNIDO and WHO and as an Advisor to Forschungszentrum Karlsruhe, T.N.O. and VITO. For 25 years, he advised the major industrial Belgian Bank and conducted more than 600 audits of enterprise.

Main activities are in thermal and catalytic processes, waste management, and flue gas cleaning, with emphasis on heavy metals, dioxins, and other semi-volatiles. He coordinated diverse national and international research projects (Acronyms Cycleplast, Upcycle, and Minidip). Dr. Buekens is author of one book, edited several books and a Technical Encyclopedia and authored more than 90 scientific publications in refereed journals and more than 150 presentations at international congresses. He is a member of Editorial Boards for different journals and book series.

He played a role in the foundation of the Flemish Waste Management Authority O.V.A.M., of a hazardous waste enterprise INDAVER, and the Environmental Protection Agency B.I.M./I.B.G.E. He was principal ministerial advisor in Brussels for matters regarding Environment, Housing, and Classified Enterprise (1989). Since 1970 he has been a Member of the Board of the Belgian Consumer Association and of Conseur, grouping more than a million members in Belgium, Italy, Portugal, and Spain.

He is licensed expert for conducting Environmental Impact Assessments (Air, Water, Soil) and Safety Studies regarding large accidents (Seveso Directive).

Nadezhda Zyaykina obtained her degree of an Environmental Engineer at The Mendeleev University of Chemical Technology of Russia, Moscow (1999) with specialization in recuperation technologies of secondary industrial materials. Then she followed a Master program in Human Ecology at Vrije Universiteit Brussel (VUB), 1999 – 2001. This interdisciplinary study of environmental problems and environmental management includes scientific, economic and regulatory approaches. Since 2001 she is doing research in the frame of a PhD program in Applied Sciences, also at VUB. The research is dedicated to analysis of adsorption/desorption properties of filter dust from various metallurgical processes in respect to dioxins and related chlorinated aromatic compounds. The investigation is also related to formation of dioxins and their surrogates by carbon gasification reactions.

Xianwei Li was born in September, 1966 in The Jiangxi Province, China. In 1984 he entered the

Undergraduate Course of The Central South University of Technology, China. He was awarded the title of Good Postgraduate Student in Three Aspects, and won the title of Excellent Graduate at graduation. His graduation thesis for a Master's Degree was "Research of a New-type Efficient Composite Burden of Medium-sized & Small-sized Blast Furnaces".

In 1991, after he received his Master's Degree, he entered the biggest iron and steel company of China, Baosteel. From 1992 to 1997, he put forward some research projects which proved to be profitable.

From 1998 to 1999, he mainly studied the pisolitic ores, such as Yandi and Robe River. The aim of the study was to increase the blending ratio of pisolite, and thus to reduce the cost of ore blending.

In 1998, he took part in the joint study projects between Baosteel and CVRD and BHP, and visited CVRD Research Center and BHP Newcastle Laboratories.

From 2000 to 2003, he studied in the field of environment as a PhD student at Tohoku University, Japan. The thesis title is Measurement and Calculation of Physicochemical Properties of Dioxin Congeners and Simulation of Their Equilibrium in Thermal Processes. He obtained his PhD in 2003, and then returned to Baosteel as a principal researcher in resources and environment.