

Adsorptive removal of volatile organic compounds from gases streams

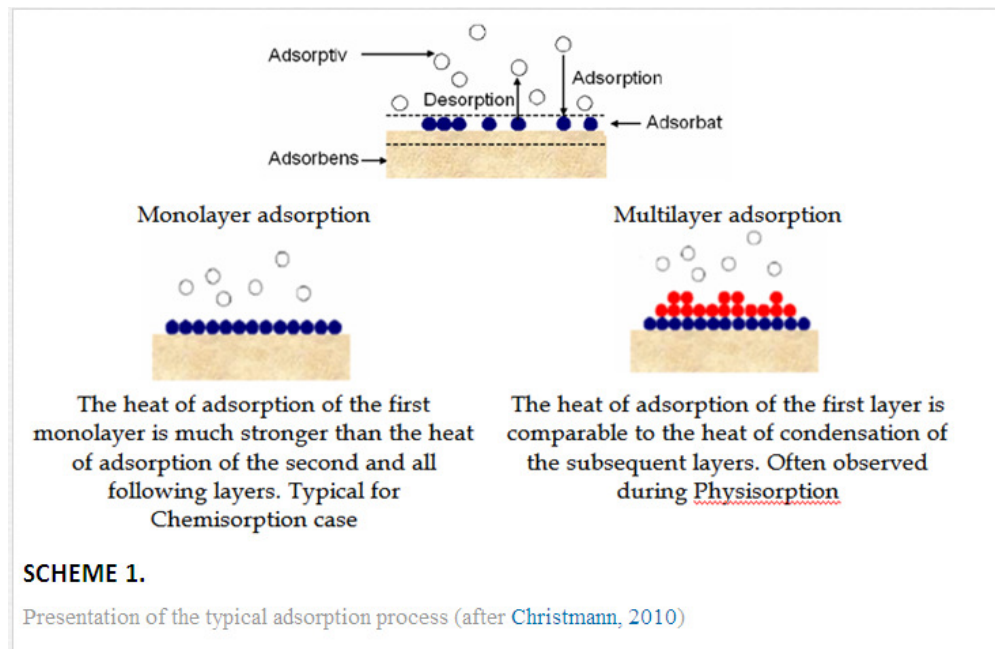
Theoretical background

Adsorption

The word "adsorption" was coined in 1881 by German physicist Heinrich Kayser (1853-1940).

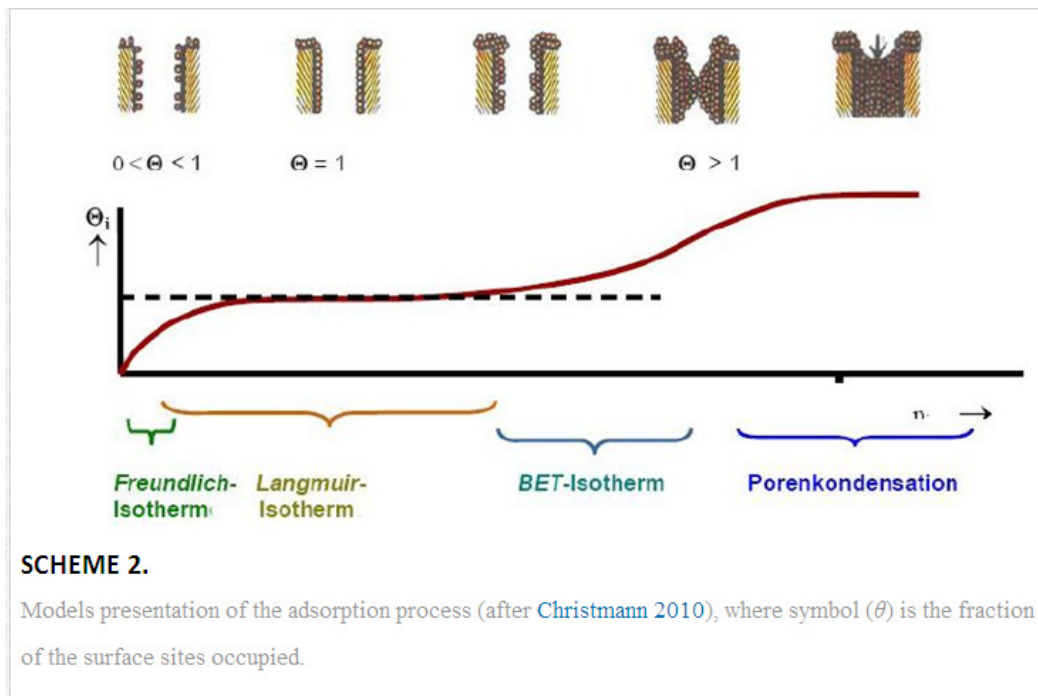
Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the *adsorbate* on the surface of the *adsorbent*. This process differs from absorption, in which a fluid (the *absorbate*) permeates or is dissolved by a liquid or solid (the *absorbent*). Adsorption is a surface-based process while absorption involves the whole volume of the material. The term sorption encompasses both processes, while desorption is the reverse of it. Adsorption is a surface phenomenon.

Schemes shown below are from paper: "Comparison of the Thermodynamic Parameters Estimation for the Adsorption Process of the Metals from Liquid Phase on Activated Carbons" by Svetlana Lyubchik, Andrey Lyubchik, Olena Lygina, Sergiy Lyubchik and Isabel Fonseca, *REQUIMTE, Faculdade Cięncia e Tecnologia, Universidade Nova de Lisboa Quinta de Torre, Campus da Caparica, 2829-516 Caparica, Portugal*



Similar to surface tension is a consequence of surface energy. In a bulk material all the bonding requirements (be they ionic, covalent or metallic of the constituent atoms of the material) are filled by other atoms in the material. However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak van der Waals forces) or chemisorption (characteristic of covalent bonding). It may also occur due to electrostatic attraction.

Adsorption is present in many natural, physical, biological, and chemical systems, and is widely used in industrial applications such as activated charcoal, capturing and using waste heat to provide cold water for air conditioning and other process requirements (adsorption chillers), synthetic resins, increase storage capacity of carbide-derived carbons, and water purification. Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column.



Isotherms

Adsorption is usually described through isotherms that is, the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass of the adsorbent to allow comparison of different materials.

The first mathematical fit to an isotherm was published by Freundlich and Küster (1894) and is a purely empirical formula for gaseous adsorbates,

$$\frac{x}{m} = kP^{\frac{1}{n}}$$

where x is the quantity adsorbed, m is the mass of the adsorbent, P is the pressure of adsorbate and k and n are empirical constants for each adsorbent-adsorbate pair at a given temperature. The function is not adequate at very high pressure because in reality x/m has an asymptotic maximum as pressure increases without bound. As the temperature increases, the constants k and n change to reflect the empirical observation that the quantity adsorbed rises more slowly and higher pressures are required to saturate the surface.

Langmuir

Irving Langmuir was the first to derive a scientifically based adsorption isotherm in 1918. The model applies to gases adsorbed on solid surfaces. It is a semi-empirical isotherm with a kinetic basis and was derived based on statistical thermodynamics. It is the most common isotherm equation to use due to its simplicity and its ability to fit a variety of adsorption data. It is based on four assumptions:

1. All of the adsorption sites are equivalent and each site can only accommodate one molecule.
2. The surface is energetically homogeneous and adsorbed molecules do not interact.
3. There are no phase transitions.
4. At the maximum adsorption, only a monolayer is formed. Adsorption only occurs on localized sites on the surface, not with other adsorbates.

These four assumptions are seldom all true: there are always imperfections on the surface, adsorbed molecules are not necessarily inert, and the mechanism is clearly not the same for the very first molecules to adsorb to a surface as for the last. The

fourth condition is the most troublesome, as frequently more molecules will adsorb to the monolayer; this problem is addressed by the BET isotherm for relatively flat (non-microporous) surfaces. The Langmuir isotherm is nonetheless the first choice for most models of adsorption, and has many applications in surface kinetics (usually called Langmuir – Hinshelwood kinetics) and thermodynamics.

Langmuir suggested that adsorption takes place through this mechanism:



where A is a gas molecule and S is an adsorption site. The direct and inverse rate constants are k and k_{-1} . If we define surface coverage, θ , as the fraction of the adsorption sites occupied, in the equilibrium we have:

$$K = \frac{k}{k_{-1}} = \frac{\theta}{(1 - \theta)P}$$

or

$$\theta = \frac{KP}{1 + KP}$$

where: P is the partial pressure of the gas or the molar concentration of the solution. For very low pressures $\theta \approx KP$ and for high pressures $\theta \approx 1$.

θ is difficult to measure experimentally; usually, the adsorbate is a gas and the quantity adsorbed is given in moles, grams, or gas volumes at standard temperature and pressure (STP) per gram of adsorbent. If we call v_{mon} the STP volume of adsorbate required to form a monolayer on the adsorbent (per gram of adsorbent),

$$\theta = \frac{v}{v_{\text{mon}}}$$

and we obtain an expression for a straight line:

$$\frac{1}{v} = \frac{1}{Kv_{\text{mon}}} \frac{1}{P} + \frac{1}{v_{\text{mon}}}$$

Through its slope and y-intercept we can obtain v_{mon} and K , which are constants for each adsorbent/adsorbate pair at a given temperature. v_{mon} is related to the number of adsorption sites through the ideal gas law. If we assume that the number of sites is just the whole area of the solid divided into the cross section of the adsorbate

molecules, we can easily calculate the surface area of the adsorbent. The surface area of an adsorbent depends on its structure; the more pores it has, the greater the area, which has a big influence on reactions on surfaces.

If more than one gas adsorbs on the surface, we define θ_E as the fraction of empty sites and we have:

$$\theta_E = \frac{1}{1 + \sum_{i=1}^n K_i P_i}$$

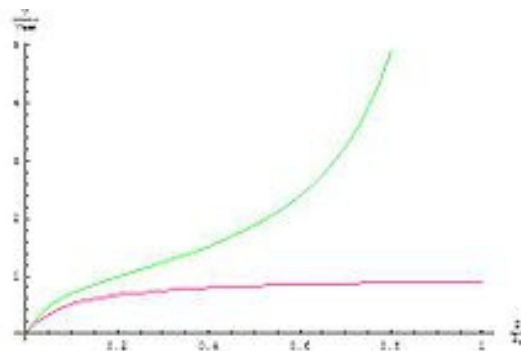
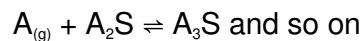
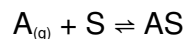
Also, we can define θ_j as the fraction of the sites occupied by the j -th gas:

$$\theta_j = \frac{K_j P_j}{1 + \sum_{i=1}^n K_i P_i}$$

where: i is each one of the gases that adsorb.

BET theory

Often molecules do form multilayers, that is, some are adsorbed on already adsorbed molecules and the Langmuir isotherm is not valid. In 1938 Stephen Brunauer, Paul Emmett, and Edward Teller developed a model isotherm that takes that possibility into account. Their theory is called BET theory, after the initials in their last names. They modified Langmuir's mechanism as follows:



Langmuir isotherm (red) and BET isotherm (green)

The derivation of the formula is more complicated than Langmuir's (see supplemented literature for complete derivation). We obtain:

$$\frac{x}{v(1-x)} = \frac{1}{v_{\text{mon}}c} + \frac{x(c-1)}{v_{\text{mon}}c}$$

x is the pressure divided by the vapor pressure for the adsorbate at that temperature (usually denoted P/P_0), v is the STP volume of adsorbed adsorbate, v_{mon} is the STP volume of the amount of adsorbate required to form a monolayer and c is the equilibrium constant K we used in Langmuir isotherm multiplied by the vapor pressure of the adsorbate. The key assumption used in deriving the BET equation that the successive heats of adsorption for all layers except the first are equal to the heat of condensation of the adsorbate.

The Langmuir isotherm is usually better for chemisorption and the BET isotherm works better for physisorption for non-microporous surfaces.

Adsorbents

Characteristics and general requirements



Activated carbon is used as an adsorbent

Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with a hydrodynamic radius between 0.25 and 5 mm. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high capacity for adsorption. The adsorbents must also have a distinct pore structure that enables fast transport of the gaseous vapors.

Most industrial adsorbents fall into one of three classes:

- Oxygen-containing compounds – Are typically hydrophilic and polar, including materials such as silica gel and zeolites.
- Carbon-based compounds – Are typically hydrophobic and non-polar, including materials such as activated carbon and graphite.
- Polymer-based compounds – Are polar or non-polar functional groups in a porous polymer matrix.

Silica gel

Silica gel is a chemically inert, nontoxic, polar and dimensionally stable (< 400 °C or 750 °F) amorphous form of SiO₂. It is prepared by the reaction between sodium silicate and acetic acid, which is followed by a series of after-treatment processes such as aging, pickling, etc. These after treatment methods results in various pore size distributions.

Silica is used for drying of process air (e.g. oxygen, natural gas) and adsorption of heavy (polar) hydrocarbons from natural gas.

Zeolites

Zeolites are natural or synthetic crystalline aluminosilicates, which have a repeating pore network and release water at high temperature. Zeolites are polar in nature.

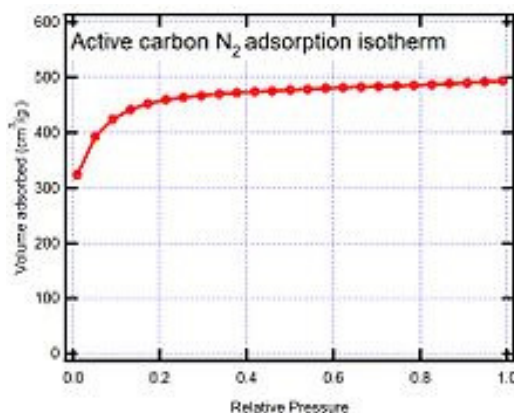
They are manufactured by hydrothermal synthesis of sodium aluminosilicate or another silica source in an autoclave followed by ion exchange with certain cations (Na⁺, Li⁺, Ca²⁺, K⁺, NH₄⁺). The channel diameter of zeolite cages usually ranges from 2 to 9 Å (200 to 900 pm). The ion exchange process is followed by drying of the crystals, which can be pelletized with a binder to form macroporous pellets.

Zeolites are applied in drying of process air, CO₂ removal from natural gas, CO removal from reforming gas, air separation, catalytic cracking, and catalytic synthesis and reforming.

Non-polar (siliceous) zeolites are synthesized from aluminum-free silica sources or by dealumination of aluminum-containing zeolites. The dealumination process is done by treating the zeolite with steam at elevated temperatures, typically greater than 500 °C (930 °F). This high temperature heat treatment breaks the aluminum-oxygen bonds and the aluminum atom is expelled from the zeolite framework.

Activated carbon

Activated carbon is a highly porous, amorphous solid consisting of microcrystallites with a graphite lattice, usually prepared in small pellets or a powder. It is non-polar and cheap. One of its main drawbacks is that it reacts with oxygen at moderate temperatures (over 300 °C).



Activated carbon nitrogen isotherm showing a marked microporous type I behavior.

Activated carbon can be manufactured from carbonaceous material, including coal (bituminous, subbituminous, and lignite), peat, wood, or nutshells (e.g., coconut). The manufacturing process consists of two phases, carbonization and activation. The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons from the raw material, as well as to drive off any gases generated. The process is completed by heating the material over 400 °C (750 °F) in an oxygen-free atmosphere that cannot support combustion. The carbonized particles are then "activated" by exposing them to an oxidizing agent, usually steam or carbon dioxide at high temperature. This agent burns off the pore blocking structures created during the carbonization phase and so, they develop a porous, three-dimensional graphite lattice structure. The size of the pores developed during activation is a function of the time that they spend in this stage. Longer exposure times result in larger pore sizes. The most popular aqueous phase carbons are bituminous based because of their hardness, abrasion resistance, pore size distribution, and low cost, but their effectiveness needs to be tested in each application to determine the optimal product.

Activated carbon is used for adsorption of organic substances and non-polar adsorbates and it is also usually used for waste gas (and waste water) treatment. It is the most widely used adsorbent since most of its chemical (e.g. surface groups) and physical properties (e.g. pore size distribution and surface area) can be tuned according to what is needed. Its usefulness also derives from its large micropore (and sometimes mesopore) volume and the resulting high surface area.

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