ADSORBENTS AND ADSORPTION PROCESSES FOR POLLUTION CONTROL

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Contents

Summary

This chapter briefly covers the major technical issues related to industrial adsorbents and their application in gas cleaning and desiccation. Fixed, moving, and fluidized bed types of adsorbers are schematically shown and their operation principles are discussed. General guidelines for an adsorber design are presented: however, they are mostly limited to the most usual case of the fixed-bed adsorber. Several approaches, based on theoretical models for calculation of breakthrough curves, are outlined. Because of the

simplifications used, it is advisable to treat these models with caution when applying them to real cases. Formulas for calculation of the essential parameters such as pressure drop and bed length are explained. Finally, the attention is drawn to some safety aspects, which should be considered while operating an adsorber.

1. Survey

Technical adsorption units are so conceived that they provide and optimize the operating conditions required for bringing the gas to be treated in close contact with an adsorbent during a sufficient time period for contact and ensure that adsorption has taken place to the required extent.

This implies that the molecules to be adsorbed may migrate to the surface, continue their path by internal pore diffusion, and adsorb. It should be noted that each of these three consecutive steps has distinct requirements, namely:

- A high relative velocity between gas and particle reduces the external mass transfer resistance and helps enhancing the migration of adsorbate towards the surface, through the laminar layer surrounding individual particles. On the other hand, high gas velocities also increase the pressure drop and reduce the residence time available in the adsorption vessel;
- Selecting adsorbent particles of a smaller size strongly increases pressure drop in a fixed adsorbent bed, but also abridges the inner pathways required for internal diffusion and increases the amount of external surface available. Disregarding the effect of pressure drop, small adsorbent particles are highly desirable. However, in practice particle size is fixed mainly by pressure drop considerations.
- A rise in temperature slightly accelerates internal diffusion. Conversely, adsorption capacity increases and residual pressure at equilibrium reduces when the operating temperature is lowered. Moreover, adsorption remains an exothermic process, which may somewhat increase the operating temperature.
- When activated carbon is used for adsorbing pollutants from air it is necessary to monitor exit temperature and/or carbon monoxide, in order to detect a possible temperature run-away and eventual ignition of the carbon.

2. Properties of Adsorbents

The most important technical adsorbents are activated carbon, which is used for almost all duties, except drying, and molecular sieves, silicagel, and alumina. Typical requirements for commercial adsorbents are:

- High porosity, high internal surface.
- High adsorption efficiency in a wide range of adsorbate concentrations.
- Good balance between macro-pores (for fast internal transport) and micro-pores (for large internal surfaces).
- Hydrophobic chemical structure (for treatment of moist gases) unless the adsorbent is to be used as a desiccant.

- Thermal stability unaffected by a cyclic regeneration.
- Mechanical integrity during handling.
- Low pressure drop over the adsorber bed.
- Low cost for acquisition (and – eventually – disposal) of adsorbents.

The most important properties of technical adsorbents are shown in the Table 1:

Apolar, low volatile organics, such as PAHs, adsorb best on activated carbon. Some inorganic vapors (e.g. mercury) can be removed efficiently by adsorption, using specially prepared, impregnated adsorbents (e.g. as a sulfide, arsenic- or antimony-compound). Activated carbon and many polymers are hydrophobic; inorganic adsorbents are hydrophilic.

Adsorbent	Nature	Average pore diameter, nm	Particle porosity, %	Surface area, $m^2 g^{-1}$	Sorptive capacity, kg kg^{-1} (dry)
Activated alumina	Hydrophilic, amorphous	4 – 14	50	320	0.1 – 0.33
Activated carbon	Hydrophobic, amorphous	1 - 4	40 - 85	200 - 1200	0.3 – 0.7
Molecular-sieve carbon	Hydrophobic, structured	0.3 – 0.6	35 - 50	400	0.2 – 0.5
Molecular-sieve zeolites	Hydrophilic, crystalline	0.3 -1	20 - 50	600 - 700	0.12 – 0.42
Polymeric adsorbents	Hydrophobic, amorphous	4 - 25	40 - 60	80 - 700	0.45 – 0.55
Silica gel	Hydrophilic, amorphous	2 - 5	47 - 71	300 - 850	0.35 – 0.5

[Values are taken from two sources: 1. Perry, R. H.; Green, D. W. eds. (1997). *Perry's Chemical Engineers' Handbook*, 7th ed., New York, NY, USA: McGraw-Hill and 2. Seader, J. D.; Henley, E. J. (1998). *Separation process principles*. 886 pp., New York, NY, USA: Wiley and combined into one table especially for this article]

Table 1: Main properties of technical adsorbents

2.1. Activated Carbon

Activated carbon is quite easy to manufacture, but much more difficult to adapt to specific applications. Traditional starting materials are charred wood, peat, lignite, or coal, but almost any organic material, including sewage sludge, animal bone, blood or hair, may be used with fair success. Production often proceeds in two either successive or overlapping steps:

1) Charring the original material, and
2) Activating it thermally or chemically in order to create the desired chemical pore structure.

Charred materials still retain the external aspects of the original feed. Charcoal, for instance still recognizably shows the cellular structure specific to the wood used. Coconut shells are a premium starting material, because of the superior crushing strength of the resulting carbonized coconut scale.

Adsorption on activated carbon is capable of a deep elimination of minor amounts of almost all low to medium volatile pollutants from a gas stream. Optimal operating conditions are:

- a relatively cold gas (optimal < 30° C),
- dry (relative humidity < 60 %), and
- dust free (particulate concentration < 1 mg m^{-3}) gas feed.

High temperatures favors desorption and thus lower adsorption capacity. The presence of water in the activated carbon or of water vapor in the adsorbate can affect the adsorption of organic gases. Molecules with a high affinity to the carbon surface, whether soluble or not, are less influenced by the presence of water. Solubility is not a dominant factor that affects adsorption on a wet carbon bed. Water vapor competes for adsorption sites and dust may clog the bed of activated carbon, if adsorption takes place in fixed bed layer.

Activated carbon can be supplied under the form of fibrous mats or even shaped filter elements. Given the supplemental cost for such conditioning these address only rather specific applications.

2.2. Specialty Impregnated Carbons

Physical forces are not always sufficient for total adsorption of a particular component. Specialty impregnated carbon refers to an activated carbon that is chemically coated or treated to enhance its adsorptivity towards specific compounds. Impregnated carbons are developed for pollutants that are difficult to control with standard activated carbons. Such adsorbents retain specific contaminants long enough for their conversion by the chemical impregnating agent, forming a stable compound within the carbon. They are used in a wide range of air, gas and water purification and industrial process applications. Some examples of contaminants removed with specially impregnated carbons are listed in Table 2.

Impregnating agent	Quantity, wt. %	Application
Sulfuric acid	2 - 25	Gas purification from ammonia, amine, mercury
Potassium carbonate	10 - 20	Gas purification from acid gases: HCl, HF, SO_2, NO_2
Manganese IV oxide	no data	Gas purification from aldehyde

Triethylene diamine	2 – 5	Gas protection from radioactive methyl iodide
Zinc oxide	10	In gas masks against hydrogen cyanide
Chromium – copper – silver salts	10 - 20	Military and civil protection: phosgene, chlorine, arsine, sarin and other nerve gases
Silver	0.1 - 3	Domestic drinking water filters

[Source: Source: adapted from http://chemistry.about.com/cs/adsorption1/index.htm. Henning K.-D.; Schäfer S. *Impregnated activated carbon for environmental protection*.]

Table 2: Applications of impregnated carbons

A typical application of such adsorbents is the reduction of mercury emissions. Even in small amounts, mercury and its compounds have an extremely harmful effect on human health. Mercury also represents a very complex problem in hydrocarbon exploration and production. Moreover, mercury corrosion attack endangers dramatically process plants and facilities. Therefore, prevention of this contaminant entering into either the biosphere or a technology-based system is absolutely critical. At least two techniques are feasible:

- Injection of powdered activated carbon into combustion flue gas, with subsequent collection in a particulate control device
- Granular activated carbon fixed-bed adsorption.

Several studies indicate that sulfur-impregnated carbons (e.g., Mersorb®, with 13 % elemental sulfur content) exhibit significantly greater mercury uptake capacities when compared to virgin carbons. The reaction results in a stable and insoluble compound, the mercury sulfide.

2.3. Zeolites

Zeolites, also called molecular sieves, are crystalline silicates with a general chemical formula $Me_{2/n}O \cdot Al_2O_3 \cdot x\ SiO_2 \cdot y\ H_2O$ (n = valence) containing oxides of alkali- or alkali-earth metals (Na, K, Ca) and characterized by regular structure of the pores with their dimensions in the range of the size of a molecule. By changing the Si to Al ratio (which is never less than 1.0, but there is no upper limit), it is possible to vary the negative charge on the framework of the zeolite.

Since each Al atom introduces one negative charge, this must be balanced by exchangeable cations. Molecular sieves with specific adsorptive properties can be produced by ion exchange or chemical treatment. An example of such a structure is given in Figure 1. Activation typically requires 300° C, applied under full vacuum or an inert purge gas.

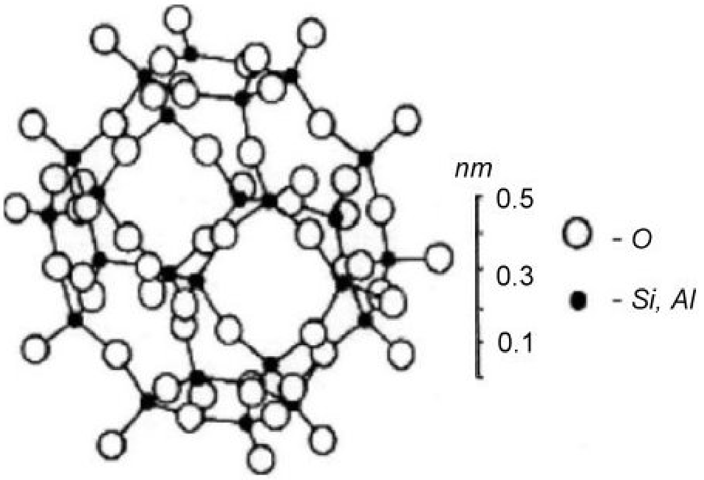

Figure 1: Structure of a molecular sieve adsorbent

Molecular sieve separations may be based on molecular size and shape because of the small pore sizes in the sieves, typically less than one nanometer, and their narrow pore size distribution.

High thermal and chemical stability make zeolites ideal materials for high temperature applications such as catalytic membrane reactors.

2.4. Silicagel

Silicagel has an amorphous structure and is described by the general formula $SiO_2 \cdot nH_2O$. The adsorption ability and chemical properties of silicagels largely depend on the presence of structural Si-OH groups at their surface. The main properties are outlined in Table 1. Silicagels are subdivided into three classes according to their pore size: large pores (≈ 5 nm) and medium pores (5 - 1.5 nm) adsorbents are used for sorption of organic vapors; small pores (1.0 - 1.5 nm) serve for removal of easy condensing vapors and gases. Generally, silicagel is used for sorption of polar compounds, especially for drying of different gaseous media. The advantages of silicagel are:

- A low temperature of regeneration: 100-200° C
- Non-flammable
- A high mechanical strength

2.5. Activated Alumina

It is produced from hydrated alumina, $Al_2O_3 \cdot nH_2O$ (n = 1-3) by dehydration under carefully controlled conditions to get n = 0.5. Common forms are balls 1 to 8 mm diameter, granules, pellets 2 to 4 mm diameter, and powder. The two widest applications of activated alumina are as a catalyst and a desiccant. It is also used as an adsorbent are for removal of oxygenates and mercaptans from hydrocarbon feed streams, fluoride ions from water, etc. It has superior mechanical strength and resistance to attrition than molecular sieves and silicagel, which is important to consider in moving bed applications. Regeneration requires heating to about 205° C.

2.6. Selection of a Suitable Adsorbent

The selection of adsorbents follows a few simple rules:

- Chemisorption is much more selective than van der Waals forces.
- The higher the molecular weight, the stronger the retention.
- Kinetic and steric effects may enhance selectivity.
- Inorganic sorbents (silicagel, alumina, molecular sieves) are particularly suitable for dehydration and for retaining hydrophilic substances.
- Organic compounds are well retained by activated carbon and less well by lignite coke.

3. Fixed bed Adsorbers

A fixed bed adsorber represents a cyclic batch system, in which the adsorbent bed is saturated and also regenerated in a periodic manner. This type of adsorption units is a standard choice for small and most medium sized installations, as well as for '*police*' filters. In the German literature this term denotes a bed of adsorbent, which is inactive under normal circumstances, but completely arrests a brief surge of a pollutant under emergency conditions.

A typical scheme is shown in Figure 2. The fixed bed adsorber consists of a steel vessel, with a distributor plate at the bottom carrying the granular adsorbent medium, and ducting for the gas feed, the cleaned gas, and the inlet and outlet for the regeneration medium (often steam). To avoid entraining adsorbent particles or even fluidizing the bed during adsorption, the flow is usually directed downwards. Regeneration proceeds in the reverse sense, so that the capacity is fully restored at the exit side of the adsorbing mode.

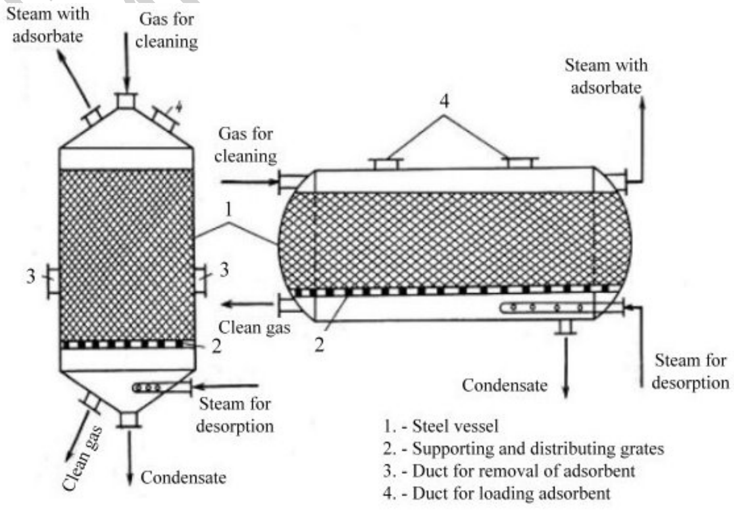

Figure 2: Scheme of fixed bed adsorber: vertical and horizontal units

Depending on space and process requirements two types of adsorber vessel can be distinguished:

- a wide version, with large cross-section. Such type is destined to cope with a large gas flow to be cleaned while maintaining a still reasonable linear gas velocity.
- a radial or annular configuration, in which an expansion of capacity takes place in the vertical rather than the horizontal direction. The latter option is much more economical in case of pressurized vessels, since the wall thickness required by mechanical strength considerations is proportional to the diameter of the vessel.

A single fixed bed adsorber can never operate on a continuous basis, since some provisions for regeneration or replacement of the adsorbent must always be made. Of course, a police filter may operate for many months before the available adsorption capacity is exhausted. Therefore, adsorption plants usually consist of several fixed bed units. This can only be avoided if the pollutant load is so low that periodic replacement and external regeneration or even disposal of the adsorbent is acceptable.

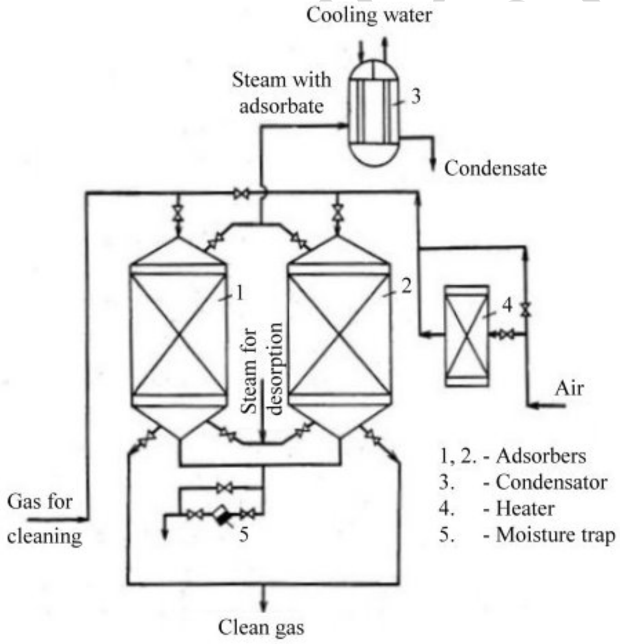

Figure 3: Operation of a two-column adsorption system

The availability of fixed bed adsorbers follows from the ratio:

$$\frac{\textit{operating time}}{\textit{time required for regeneration}}$$

The numerator is substantial, because the bed must be not only regenerated thoroughly, but also dried and cooled before returning to activity. Before or during breakthrough the active bed unit is taken out of service for regeneration and replaced by another one, with its adsorbent already treated.

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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.