ADSORBENT SELECTION

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1. Introduction

Adsorption can perform many separations that are impossible or impractical by conventional techniques, such as distillation, absorption, and even membrane-based systems. Lately, applications for adsorption have expanded rapidly because of sharply rising environmental or quality requirements. Likewise, advances in adsorbent technology have made it possible to meet many of those demands. Recently developed adsorbents are now available "off-the-shelf," and in most cases they can perform satisfactorily. Nevertheless, new adsorbents are constantly being synthesized that have dramatically improved properties which translate into better performance. A new adsorbent may take months or years to perfect, however, so a rule-of-thumb is that there is never enough time to develop a new adsorbent for an urgent new application.

Going hand-in-hand with these advances, engineers and scientists have developed a better understanding of the mechanisms of adsorption. In fact, this has led to faster and more accurate simulations and designs of adsorption processes. For the past thirty years, it has been possible to solve the relevant equations numerically. Recently, that ability has been augmented by faster, more accessible machines, as well as models that are able to isolate the relevant effects without being bogged down by too many fitted parameters.

This article presents the basic principles of adsorption, emphasizing practical aspects of adsorbent selection. After this introduction is a brief qualitative description of common adsorbents, followed by an overview of important, quantitative adsorbent characteristics, and finally some case studies illustrating the main ideas. There is not sufficient space here to review adsorption technology or adsorber design, although just as much could be said about them. For that matter, most of the topics discussed here are the subject of dozens of technical papers each year. Some subjects are treated in much greater detail by specialized books and/or journals, including adsorption itself, along with carbon, zeolites, reactive polymers, and others.

Perhaps the best known applications of adsorption fall in the category of purification, e.g., municipal water treatment to remove traces of pollutants, as well as "taste" or "odor." Another widespread application, although much smaller in terms of adsorbent consumption, is the pressure-swing air dryer found on semis for their air-brake systems. (Most of us have heard the abrupt, loud "blowdown" of one of these adsorbers and have wondered if one of our tires blew-out. Moments later we realize that instead it was "something" under the truck.) Adsorption is becoming more popular as a unit operation, as a means for separating fluid mixtures. For example, adsorption is used to recover very pure para-xylene from mixed isomers in a well known process called Parex®, offered by UOP. Likewise, pressure swing adsorption (PSA) is commonly used to split very pure hydrogen from refinery off-gases.

There exist hundreds, if not thousands, of different applications of adsorption (Yang, 1987), but we are looking at adsorbent selection rather than process selection. Thus, the point of citing the above examples is not just to illustrate the diversity of operations. Rather, it is to highlight the vastly different *priorities* of adsorbent properties for those applications. All require a degree of effectiveness, usually thought of as high adsorption capacity, coupled with high selectivity. In many cases the adsorption rate and pressure drop are also important; hence, particle size is important. Besides those, nearly every different application has a different set of additional priorities. For example, the main prerequisite for municipal water purification is low cost. Fortunately, activated carbon offers both low cost and high effectiveness and no other adsorbents are close. The choice would be easy, except that there are many activated carbon manufacturers, and each of those typically offers several products. Conversely, there are many potential classes of desiccants for pressure swing air drying, including: activated alumina, silica gel, zeolite, anhydrous calcium sulfate, and even polymeric adsorbents. To be placed on-board a truck chassis, and undergo the vibration, temperature extremes, etc. that are experienced by cross-country rigs, however, adds a few additional constraints. Attrition resistance and protection from oil and exhaust gases are chief among them. We will continue this line of thought below, but in a broader and more objective way that applies to a wide variety of applications and adsorbent materials.

Since this article deals with adsorbent selection, it is appropriate to comment briefly on the procedure, instead of just the technology. The first task is to define the purpose of the adsorbent or adsorption system. Until one does that, comparing performance specification or properties is a waste of time. To illustrate, recently I received a phone call from a fellow who loosely described an application. He then said, "We've tentatively chosen activated carbon, probably coconut shell-based, because its "standard" toluene isotherms are better than the others. He had mentioned odors and noxious fumes but nothing about aromatic hydrocarbons, so I naturally asked why that particular characteristic was so important. There was a long pause, after which we made progress. The point was that someone selling *XYZ Adsorbent* had convinced him that it was best because of its toluene adsorption isotherm, without explaining the correlation of that property to his application. It goes without saying that most people who sell adsorbents or equipment, do not make a living by offering unbiased advice. Generally, if they do not leave you with the impression that their products are superior, they have not done their job well. So, the goal of this article is to help you understand what is important, and how to express it, without being swayed by sales tactics alone.

The opposite extreme is not much better, which is to assume that any class of adsorbent is a likely match, and that within any class there are several candidates offered by each manufacturer. This approach can lead to a sea of data, so that the initial goal gets lost. It would, however, lead to full employment for laboratory technicians and those skilled at spreadsheets for data analysis.

When discussing process alternatives in this article, it is presumed that regeneration in-place is desired. These days it is becoming rare, for several economic, environmental and technical reasons, to propose a system in which the adsorbent is discarded, e.g., in a landfill, after one use. Off-site regeneration or reactivation is still common for activated carbon, however.

2. Adsorbents: Classes, Sources, Properties and Applications

This section explains the general characteristics of adsorbents, and why they are important. The following parts deal with classes of adsorbents and several common materials are mentioned, along with a few manufacturers and some typical applications. No attempt has been made to be exhaustive in any lists. Many obvious examples have undoubtedly been omitted. The most important attributes of an adsorbent for any application are: ***capacity***, ***selectivity***, ***regenerability***, ***kinetics***, ***compatibility***, and ***cost***. Rarely will a single adsorbent be optimal in all these respects. Frequently it will be possible to narrow the choice to one or two classes of adsorbents, but that still commonly leaves a vast array of possibilities.

To evaluate capacity, selectivity, regenerability, kinetics, compatibility, and cost, a number of different approaches can be taken. First, vendors can be contacted, and if the compound is relatively common, they may be able to provide information quickly. Otherwise, especially for a relatively large application, they may be willing to do measurements. Second, you might use a database, such as one that was mentioned earlier in this article. Third, you might arrange to conduct the measurements, either yourself or by someone else in your firm. Fourth, you might arrange to have tests conducted by an independent firm, since they could offer an unbiased and cost efficient assessment.

Adsorption ***capacity*** (or "loading") is the most important characteristic of an adsorbent. Simply stated, it is the amount of adsorbate taken up by the adsorbent, per unit mass (or volume) of the adsorbent. It depends on the fluid-phase concentration, the temperature, and other conditions (especially the initial condition of the adsorbent). Typically, adsorption capacity data are gathered at a fixed temperature and various adsorbate concentrations (or partial pressures for a vapor or gas), and the data are plotted as an *isotherm* (loading versus concentration at constant temperature). Adsorption capacity is of paramount importance to the capital cost because it dictates the amount of adsorbent required, which also fixes the volume of the adsorber vessels, and both generally are significant if not dominant.

Speaking of isotherms, there are only a handful of shapes (some are shown in Figure 1), but there are dozens of empirical forms, some of which are discussed later in this article. Beyond those, there exist many other means to express adsorption capacity: isosteres, isobars, and various indices, such as surface area, pore size distribution, Iodine Number and Molasses Number. The latter two are used exclusively to describe activated carbons. Isosteres and isobars, along with isotherms, are discussed more fully later in this article. Surface area is a relative term, usually measured by inferring the monolayer coverage within an adsorbent of a substance with known density and molecular dimensions (e.g., nitrogen near its normal boiling point). Values typically correlate with capacity, and for various adsorbents are in the range of, say, 5 to 3,000 m^2/g. Related to the weight of a penny (2.5 g), the range is from a 12 ft x12 ft square to nearly two football fields! Some specific ranges are listed for common adsorbents in the next section. Surface area alone is not a proper basis for choosing an adsorbent.

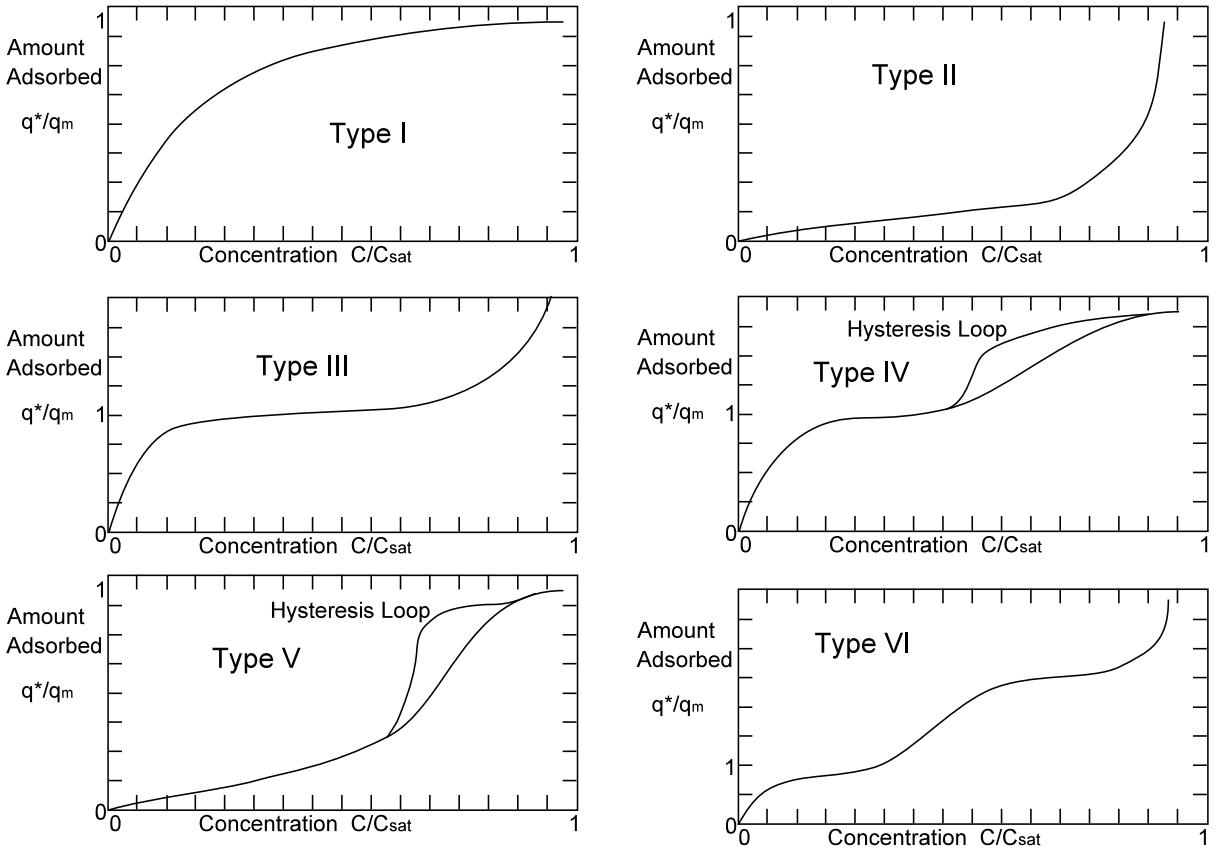

Figure 1. Classic Isotherm Types.

The pore size distribution is a related property that indicates the fraction of the space within a particle occupied by micropores ($d_p < 20Å$), mesopores ($20Å \le d_p < 500Å$), and macropores ($d_p \ge 500Å$). Pore dimensions intuitively correlate with both capacity and kinetics, but the exact dependence is subtle. Figure 2 shows the pore size distributions of some common adsorbents. The Iodine Number is a rough measure of capacity for small molecules and correlates with surface area. The Molasses Number was developed for decolorization of cane sugar, and relates to adsorption of large molecules from a liquid. Sometimes people selling adsorbents will use terms like these, possibly not realizing that we do not use them everyday, as they do. It never hurts to ask, "What does that term mean to my application?"

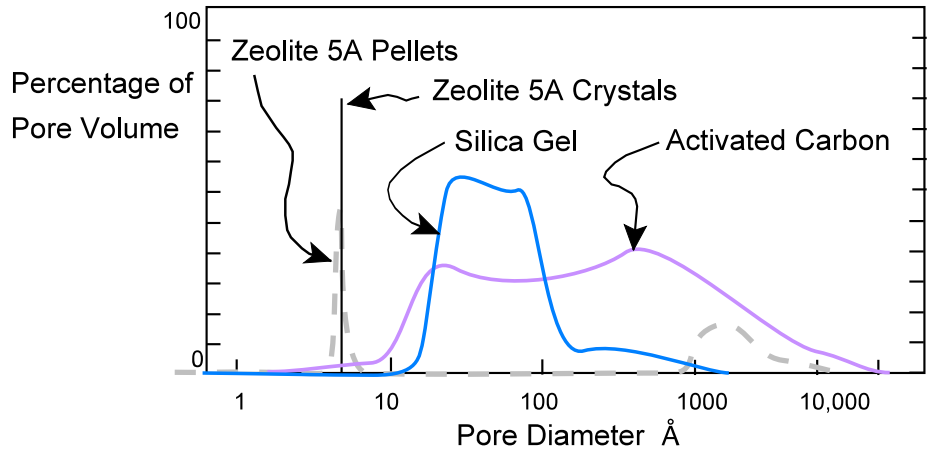

Figure 2. Pore Size Distributions of Common Classes of Adsorbents.

Figure 3 illustrates how pore sizes relate to sizes of common, simple molecules and elements. It shows the Lennard-Jones (6-12) collision diameters along with micropore diameters of some common adsorbents. For many of the common adsorbents only a minimum pore size is shown (ignoring the average and range), while for molecular sieves the nominal micropore size is shown (ignoring the macropores).

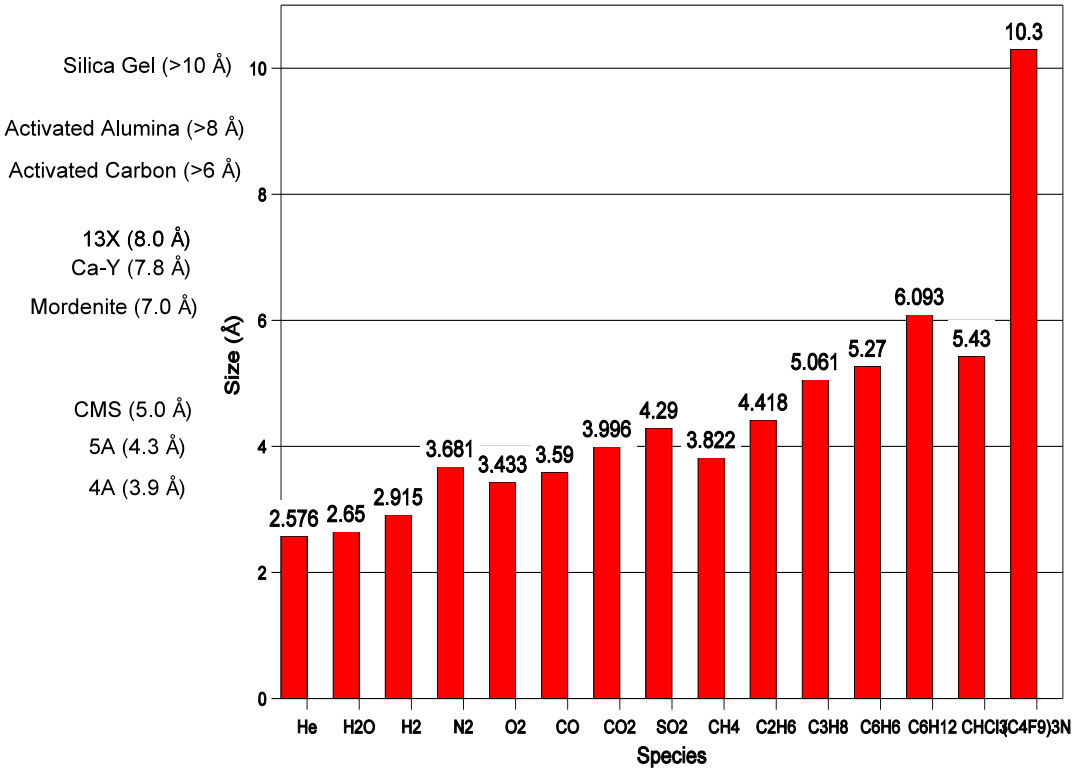

Figure 3. Typical Pore Sizes and Effective Sizes of Common Molecules.

Selectivity is related to capacity, but there are several distinct definitions that will be discussed later in this article. The simplest is the ratio of the capacity of one component to that of another at a given fluid concentration. That ratio generally approaches a constant value as concentration drops towards zero. Of course, the concentrations of interest may not be near zero, so the choice of definitions becomes subtle. The closest analogy is to relative volatility (e.g., in distillation) in that the smaller the value, the larger the required equipment. An ideal situation occurs when the major component is not adsorbed much (so it can be thought of as an inert "carrier"), which leads to a very large selectivity. Some people prefer a bounded selectivity (i.e., 0 to 1), and they employ the inverse of the ratio mentioned above. Thus, it is a good idea to clarify the definition first, or to speak of "good" or "bad" instead of "large" or "small."

All cyclic adsorption applications rely on ***regenerability***, so that the adsorbent can operate in sequential cycles with uniform performance. This means each adsorbable component (adsorptive or adsorbate) must be relatively weakly adsorbed (or physisorbed). The heat of adsorption, which is mentioned later, provides a measure of the energy required for regeneration, and in that regard low values are desirable. Regeneration might be accomplished by a thermal swing, pressure swing, chemical (e.g., by displacement, elution, or supercritical extraction), or sometimes by a combination of those. Displacement would involve introducing a species that adsorbs more strongly than the adsorbate of interest, while elution would entail dissolving the adsorbed material by a solvent that is weakly adsorbed if at all. The chemical methods all require a separate separation operation that may be costly, plus a means must be found for purging the bed of the regenerant. In some cases, regeneration takes place by contacting the adsorbent with a fluid in another phase than is used during loading. This requires draining or displacement which might be time-consuming, so it is avoided whenever possible. The regenerability of an adsorbent affects the fraction of the original capacity that is retained (sometimes called the *working capacity*), and the time, energy, etc. required for regeneration. Frequently, a short-term loss of working capacity occurs during the first few cycles, often followed by a gradual decay, perhaps over hundreds of cycles, e.g., due to ageing, poisoning, or other causes unrelated to regeneration, that essentially governs the life of the adsorbent.

Mass transfer ***kinetics*** is a catch-all term related to intraparticle mass transfer resistance. It is important because it controls the cycle time of a fixed bed adsorption process. Fast kinetics provides a sharp breakthrough curve, while slow kinetics yields a distended breakthrough curve. The effect of a distended breakthrough curve can be overcome by adding adsorbent at the product end, or by increasing the cycle time (which reduces the throughput per unit of adsorbent). Both of these options affect the amount of adsorbent required in that the longer the cycle time, the greater the adsorbent inventory. Despite that, kinetics has even been exploited as the basis of adsorptive separations. Perhaps the most common example is the pressure swing adsorption process that splits nitrogen from air using carbon molecular sieve, which relies on fast diffusion of oxygen compared with very slow diffusion of nitrogen. Normally, however, slow diffusion of any adsorbate is a disadvantage. To compensate for slow diffusion, it is also possible to use small particles, but there is a corresponding sacrifice due to increased pressure drop. The common solution to that dilemma is to use relatively large particles and to employ an extra increment of adsorbent.

Compatibility covers various possible modes of chemical and physical attack that could reduce the life expectancy of the adsorbent, such as biological fouling or attrition. For example, the adsorbent, binder, and surface groups (depending on the type of adsorbent), should be inert to the carrier or solvent, and should not irreversibly react with (or chemisorb) the adsorbate(s) or contaminants. Likewise, operating conditions such as velocity, temperature, pressure, and vibration should not cause undue disintegration of the adsorbent particles. This could happen by crushing or abrasion, and there are standard methods for measuring those.

Cost is perhaps the most subtle characteristic to understand because it may vary from week to week, and from sales rep to sales rep, even for the same exact material. Prices range from $0.30 per pound to $50 per pound for materials that are not particularly exotic.

2.1. Inorganic Materials

It seems that most minerals and many synthetic inorganic materials have been tried as adsorbents. Some have been successful, despite being poor adsorbents, simply because they were so inexpensive. Others have turned out to be immensely effective adsorbents. Conversely, some inorganic materials may act more as "absorbents" than adsorbents, but have applications from drying to recovery of PCBs. Among these are metal chlorides ($CaCl_2$), oxides (CaO, MgO, ZnO for life support in the space program), silicates ($MgSiO_3$), sulfates ($CaSO_4$, the familiar "Drierite"), kieselguhr (or diatomaceous earth), and even sodium bicarbonate and limestone (for flue gas treatment). Some are used in an anhydrous state while others are hydrated. Many other inorganic adsorbents have been developed recently, such as pillared clays, aluminophosphates, and mesoporous adsorbents, that have not yet achieved that level of prominence. The inorganic adsorbents covered below are commercial products, and are frequently encountered. Those included here are listed in alphabetical order, rather than by importance.

aluminas Activated alumina is produced from hydrated alumina, $Al_2O_3 \cdot n\ H_2O$, where n=1 or 3, by dehydration (calcining) under carefully controlled conditions to get $n \approx 0.5$. It is a white or tan, opaque material that has a chalky appearance. Several grades of are produced by various manufacturers, including Alcan, Alcoa, Lonza, Rhône-Poulenc, and UOP. The distinctions are in the crystal structure of the alumina. Stable crystalline forms are usually not thought of as adsorbents due to their low surface areas. Conversely, transitional forms, such as gamma and eta alumina, have defect spinel forms which lead to higher concentrations of surface acid sites. Corresponding effective surface areas are from 200 to 400 m^2/g. Common forms are balls 1 to 8 mm dia., granules, extrudates (pellets) 2 to 4 mm dia., and powder. The two widest uses of activated alumina are as a catalyst (or catalyst support) and as a desiccant. Ancillary uses as an adsorbent are for removal of: oxygenates and mercaptans from hydrocarbon feed streams, fluoride ions from water, HCl from hydrogen in catalytic reforming, and others. Pretreatment, for most gas-phase applications, requires heating to about 250°C.

silicas Silicas are generally clear or faintly tinted, and transparent or translucent. Some silica gels, however, are manufactured with alumina blended in, and this yields an appearance of alumina, viz., opaque and white or tan. Several forms are available that encompass diverse types of silica gel, porous boro-silicate glass, and aerogels. The last is a relatively new, exceedingly porous material for which few commercial applications exist. Its unique characteristics make it an interesting prospect for the future. Silica gel and porous glass are both non-dusting and resistant to attrition. Although there are seventeen crystalline varieties of SiO_2, the former can be thought of as a rigid (but not crystalline) assemblage of spherical microparticles made of colloidal silica. The latter is an open-celled porous glass. Manufacturers include the Davison Chemical Division of W.R. Grace, Engelhard Process Chemicals, Rhône-Poulenc, and Zeochem. Effective surface areas range from 300 to 900 m^2/g, depending on the density, with more dense materials having finer pores and larger surface areas. Common forms are beads 1 to 3 mm dia., granules, extrudates (pellets) 2 to 4 mm dia., and powder. The widest uses of silica gel and porous glass are as a desiccant. Ancillary uses as an adsorbent are for separation of hydrocarbons, dewpoint reduction for natural gas, and drying of liquid hydrocarbons. Pretreatment, for gas-phase applications (especially as a desiccant), requires heating to about 200°C.

zeolites Most zeolites are aluminosilicates which could be thought of as stoichiometric blends of the two previous adsorbents, silica and alumina. Thus, they are generally white, opaque and chalk-like in appearance. One would think that given their make-up, all zeolites would be hydrophilic. Accordingly, most that have significant alumina content are hydrophilic, while those that are predominately silica are hydrophobic. Internally, zeolites are inherently crystalline and exhibit micropores within those crystals that have uniform dimensions, as depicted in the pore size distribution shown in Figure 2. The micropores are so small and uniform that they commonly can distinguish nearly identically sized molecules. As a result they have been called "molecular sieves." As mentioned earlier, Figure 3 illustrates that point, showing the

Lennard-Jones (6-12) collision diameters of several simple molecules along with the micropore diameters of some common zeolites. One compound that is not shown is perfluorotributylamine, though it is one of very few that is larger than the micropores (~12Å), so it can be used to ascertain particle properties by immersion. Frequently there is water of hydration within the crystals, and in order to balance the charges, cations are associated with the alumina. The common empirical formula for a zeolite containing a single cation, M, of valence, n, is: $M_{2/n} \bullet Al_2O_3 \bullet x_{Sit} \bullet y\, H_2O$, where x is the silica-to-alumina ratio (generally ≥ 1 to 5), and y is the molar water of hydration.

Virtually all commercial, zeolitic adsorbents are composites of very fine crystals held together with a corresponding binder. Surprisingly, some types of binder can exhibit substantial adsorption capacity, yet retain strength. To the chagrin of most people who are familiar with adsorption in carbon, the adsorption capacity of zeolites is due to micropores that are so small and curved that it is not useful to express an effective surface area. To promote crystal uniformity, most commercial zeolites are synthesized in autoclaves in which conditions can be controlled tightly. The resulting crystals exist in a metastable form, and more than one hundred distinct forms have been produced. Only a handful are commercially significant (e.g., A, X, Y, ZSM-5, mordenite and silicalite), although those have different "exchange" forms and are produced in different sizes and shapes. Some of the variety is summarized in Table 1. Manufacturers include: Ceca, Davison/WR Grace, Tosoh, UOP, and Zeochem. Particle selection includes: 1 to 6 mm dia. extrudate, 0.5 to 3 mm beads, 20x40 to 6x12 mesh, and powders. Applications of zeolites include gas or liquid drying, separation of oxygen from air, normal paraffins from naphtha, and p-xylene from other isomers. Activation for gas-phase applications typically requires more stringent conditions than for silica or alumina, viz., 300°C under full vacuum or an inert purge gas.

Table 1. Commercial Zeolite Characteristics

Zeolite Type	Cationic Form	Nominal Pore Diameter (Å)	Si / Al
3A	K	3	1
4A	Na	3.9	1
5A	Ca	4.3	1
10X	Ca	7.8	1.2
13X	Na	8	1.2
Y	K	8	2.4
Mordenite	Na	7	5
ZSM-5	Na	6	31
Silicalite	-	6	∞

2.2. organic materials

This section discusses adsorbents that are based on organic material, whether synthetic or naturally occurring. A wide variety of organic materials have been used as for "sorption," besides activated carbon or charcoal. Some might function as solid "absorbents" rather than adsorbents. Among these are cellulose (the most abundant biopolymer in nature), chitin (the second most abundant biopolymer in nature), collagen, wool, starch-polyacrylamide gels (which absorb many times their own weight of water at ambient temperature, but release most of it by gentle heating), polysaccharrides derived from corn, and miscellaneous forms of biomass (e.g., residue from crop harvests). Some of these may have niches, but none would be considered a general purpose adsorbent. Here we will focus on commercial adsorbents.

activated carbon Although the choices among zeolites are immense, activated carbons are even more diverse. For example, the base materials that comprise activated carbons include: wood, coal, peat, coconut shells, saran, recycled tires, and others. The final adsorbents all look, to the casual observer, pretty much the same, i.e., black granules or pellets, but appearances can be deceptive. Activation produces a distribution of internal pores, and affects the carbon surface (e.g., graphitic versus oxidized), generally to enhance its adsorptive capacity. Thus, by varying activation conditions, differences of the internal surfaces can be induced, even for materials that appear to be identical. Another feature that varies, depending on the nature of the base material, is ash content, which is of course inorganic. Typical values are between 2 and 25%, but the average is about 7%. Alkali ash near or at the surface can be removed by acid washing or other minerals may be deposited by impregnation. The microscopic structure (pore size distribution and surface area), surface qualities, and chemical composition all strongly affect adsorption characteristics, and they therefore affect the performance parameters (capacity, selectivity, regenerability, kinetics, compatibility, and cost). In fact, there are so many variables that it is surprising that firms are able to maintain specifications of specific products, through tight quality control.

Manufacturers include Waterlink - Barnebey - Sutcliffe, Calgon, Ceca Division of Elf Atochem, Kansai Coke & Chemicals, Norit, Showa Denko, and Westvaco. Effective surface areas generally range from 300 to 1,500 m^2/g, depending on the base material, activation method, density, etc., although some made from petroleum coke exceed 3,000 m^2/g. Surface areas are treated about the same as engine horsepower or displacement are for automobiles: those with the largest tend to imply that they are the best. Assuming that area correlates with capacity, and that all other factors are equal, that assertion might be valid. Otherwise, it is prudent to make an objective assessment of all the performance criteria.

Common forms are beads 1 to 3 mm dia., granules, extrudates (pellets) 2 to 4 mm dia., and powder. Some typical applications are: water and wastewater treatment to remove hazardous organic compounds or those that impart odor or taste, cleanup of off-gases containing volatile organic compounds (especially solvents which might be recovered, and odoriferous chemicals which are merely trapped), upgrading methane from substandard natural gas wells, food decolorization, and pharmaceutical purification. Impregnated activated carbons are widely used in gas masks and to remove other specific contaminants in gas or water. Impregnants include sulfuric acid (for ammonia or mercury), iron oxide (for hydrogen sulfide or mercaptans), zinc oxide (for hydrogen cyanide), and a combination of heavy metal salts (for phosgene, arsine, and nerve gases). Pretreatment for gas-phase applications is often performed as the last step of manufacture, due to the large quantities employed because it would be impractical to do on-site. requires heating to about 200°C.

Adding to the diversity is a relatively new type of product called a "carbon molecular sieve," analogous to the zeolite molecular sieve mentioned before. While micropores in zeolites tend to have rounded apertures, the carbon-based counterparts are more slit-like, as in the space between layers of graphite. To date, only one type of commercial separation employs this material: separation of nitrogen from air. This pressure swing process exploits the difference between sizes of oxygen (3.43Å) and nitrogen (3.68Å), and can achieve 99.9% nitrogen purity.

polymers Polymeric adsorbents tend to be opaque spherical beads, but the color depends strongly on the product. Most commonly they are white or tan, but some are brown, orange, or black. The first materials were originally the inert particles that would otherwise have been further treated to make macroporous or macroreticular ion exchange resins. As such, they were typically polystyrene/divinylbenzene copolymers having a spherical shape and high pore volume. Some are still that sort of byproduct, but most are manufactured separately, with high performance in adsorption as their purpose. Internally, the polymer beads contain "microbeads" that are joined together at a few points each, creating a macropore structure. Each microbead is usually comprised of a gel, but may be made porous. In addition, some polymeric adsorbents are activated via pyrolysis, in much the same way as carbon (yielding the black materials alluded to above), yet the particles retain their strength and spherical shape. Manufacturers include Bayer, Dow Chemical, Hayes Separations, Mitsubishi, Purolite, and Rohm and Haas.

Instead of being limited to styrene/divinylbenzene, polymeric adsorbents are also made from polymethacrylate, divinylbenzene/ethylvinylbenzene, or vinylpyridine and are sometimes sulfonated or chloromethylated, much as are ion exchange resins. As a result, some are sufficiently hydrophilic to be used as a desiccant, while others are quite hydrophobic. The effective surface area is usually smaller than for activated carbon, e.g., 5 to 800 m^2/g. The corresponding pore diameters range from about 20 to 2,000 Å, or from 3 to 2000 Å if activated. The available forms are fairly limited: beads of 0.3 to 1 mm dia., usually in a relatively narrow range. Obtaining even smaller particles would not be a problem, since they are even used for gas chromatography, but larger particles are not yet commercially available. A minor drawback of these materials is that they tend to shrink and swell upon cyclic use. For gas-phase applications they may require conditioning prior to use, e.g., washing with water and/or another solvent followed by drying.

The range of applications is somewhat restricted, since the cost of most polymeric adsorbents is typically about 10× that of others that are available. In some instances other adsorbents simply cannot perform, so polymeric materials are the only choice. In other cases they compensate for the cost differential by yielding much better performance, especially for high value-added uses. Current applications include: recovery and purification of antibiotics and vitamins, decolorization, decaffeination, hemoperfusion, separation of halogenated light organics from water, and treatment of certain industrial wastes such as aqueous phenolics and VOC recovery from off-gases.

3. Adsorption Characteristics

This section describes the scientific and quantitative characteristics of adsorbents for specific applications. The properties discussed here are only those relevant as a basis for adsorbent selection. Others, which may be only indirectly relevant, are glossed over. In fact, the material presented here is just an overview, since to understand their impact requires fairly deep understanding of the field of adsorption.

3.1 Adsorption Equilibrium and Heats of Adsorption

The concept of adsorption equilibrium is involved deeply in the measurement and correlation of adsorption capacity, selectivity, and regenerability data. Generally, equilibrium is the constraint that limits each of these vital factors for every adsorption application. Earlier in this article, the term adsorption capacity was used freely as the amount of adsorbate taken up by the adsorbent, per unit mass (or volume) of the adsorbent. The following general definition expresses the relationship with as an arbitrary function of partial pressure or concentration and temperature.

$$n_i^* = f(p, T)\big|_T \quad or \quad = f(C, T)\big|_T \tag{1}$$

In the next section we will see specific functions that are commonly used to represent data. From here on, we assume that proper pretreatment has been done. Even so, there may be other conditions that affect equilibrium, especially the presence of other compounds that may compete for space in the adsorbent, or may adsorb irreversibly and reduce the effectiveness of the adsorbent.

Adsorption equilibrium is a branch of thermodynamics. As such, there is a scientific and mathematical basis for observed properties and interactions, but that goes far beyond the purpose of this article. We can omit the derivations and settle for a brief verbal description, then move on to useful relationships. As a point of reference, most of the fundamental equations have direct analogies to vapor-liquid equilibrium and simple gas laws. To cite just one example, adsorbed material is frequently viewed as a 2-dimensional fluid that exhibits a "spreading pressure" instead of a partial pressure, and there is a corresponding sort of ideal gas law, but it is called "ideal adsorbed solution" theory, which was developed by Myers and Prausnitz. Equilibrium calculations mainly involve the interactions of one molecule (or atom) of adsorbate with the adsorbent surface. This viewpoint is known to be valid only in the most idealized conditions. Normally, the surface is irregular or heterogeneous (both energetically and geometrically), which can be taken into account by many theories, and the adsorbed molecules (or atoms) interact with each other via mutual repulsion (or sometimes attraction).

As mentioned above, equilibrium data can be presented and used in a variety of forms: isotherms (loading versus concentration at constant temperature), isosteres (partial pressure {or dewpoint, or some other form of concentration} versus inverse absolute temperature at specific degrees of loading), and isobars (loading as a function of temperature for given partial pressures {or some other concentration}), listed in order of decreasing prevalence. The object of isosteres and isobars is usually to plot them on coordinates for which approximate linearity is expected, to make interpolation and extrapolation easier.

Selectivity describes, in the simplest possible form, the nature of multicomponent equilibria. Some common definitions are:

$$\alpha_{ij} = \frac{y_i / y_j}{x_i / x_j} \qquad (2) \qquad\qquad \alpha'_{ij} = K_i / K_j \qquad (3)$$

$$\beta_{ij} = \frac{1 + \frac{1-\varepsilon}{\varepsilon} K_j}{1 + \frac{1-\varepsilon}{\varepsilon} K_i} \qquad (4) \qquad\qquad \beta' = K_j / K_i \qquad (5)$$

The variables, x_i and y_i, are the mole fractions in the fluid and adsorbed phases, respectively. It is easy to measure the former but tedious to determine the latter. In addition, the ratio usually varies as the fluid composition varies, so eq.(2) is frequently used because it is constant at a given temperature. The latter equation uses isotherm slopes at the limit of zero concentration, K_i (also called the Henry's law coefficient), and conventionally the first component, "*i*," is more strongly adsorbed than component "*j*." In that case, α and α' vary between unity and infinity, as does relative volatility, while β and β' vary between zero and unity. Again when discussing results, it is a good idea to clarify the definition first, or to speak of "good" or "bad" instead of "large" or "small."

The term *regenerability* was also referred to previously without saying exactly what it means. To do so implies choosing the regeneration method. Regenerability would then revolve around the isotherm (or loading) under the process conditions versus during regeneration. For a temperature swing cycle, this would mean looking at the appropriate isotherms for uptake and release, and assessing the change of loading. Likewise, for chemical regeneration, e.g., by displacement or elution, or for a pressure swing cycle, it would mean looking at the loading under the relevant conditions. Of course, kinetics could affect the ability to attain those loadings, but that is covered later.

The heat of adsorption is a measure of the energy required for regeneration for gas or vapor phase applications, and low values are desirable. It also provides an indication of the temperature rise that can be expected due to adsorption under adiabatic conditions. Again, there are several definitions: isosteric, differential, integral, and equilibrium, to name a few. The most relevant (because it applies to flow systems instead of batch systems), is the isosteric heat of adsorption, which is analogous to the heat of vaporization and is a weak function of temperature. The definition is:

$$q_{st} = -R\left[\frac{\partial \ln p}{\partial (1/T)}\right]_{n^*} \qquad (6)$$

where p and n, respectively would be total pressure and loading for a pure gas, or partial pressure and component loading for a mixture. Besides an indication of the energy required for regeneration, this term shows how the adsorbate interacts with the adsorbent. To illustrate, a plot of isosteric heat of adsorption versus loading generally follows one of three trends: monotonically decreasing, increasing, or constant, as loading increases. The first case indicates that adsorption is strong at low concentrations, possibly due to a heterogeneous surface at which the "strong" sites are filled first. The net effect is that regeneration is likely to be difficult. The second case indicates the reverse, and regeneration is likely to be relatively easy, especially if the heat of adsorption is also low. The third case is neutral.

3.2. Isotherm Equations

As said earlier, equilibrium capacity (or "loading") data over a range of fluid-phase concentrations (or partial pressures for a vapor or gas), and at a fixed temperature, constitute an isotherm. Since those data will normally be used to design or fill a vessel, it is appropriate to cite measured densities, too. That will make it possible to relate the dimensions to cost, assuming the adsorbent is sold on a weight basis. Many of the equations that are used to fit isotherm data are semi-theoretical, and those having more parameters can account for more subtle effects. In most cases simpler is better. Occasionally, however, subtle variations in isotherm data are evidence of not-so-subtle interactions that can cause significant effects in column operations. Therefore, be cautious about oversimplifying, and avoid focusing only on gross behavior. Outright predictions are currently impossible, so it is always necessary to obtain data under relevant conditions. Brunauer, Deming, Deming, and Teller observed that isotherm data followed patterns, i.e., Types I-V shown in Figure 1. They also suggested a powerful, but complex equation (referred to as the BDDT equation) that has four parameters and can fit all the forms.

Dozens of other pioneers have devised clever equations (generally more empirical) that fit those shapes, often accounting for seemingly minor distinctions in the data. Several are discussed by name in the next two sections. These typically apply to Type I , II or IV data, which represent "favorable" equilibrium (concave downwards). The others, Types III and V, represent "unfavorable" equilibrium, and no one wants to use an adsorbent that exhibits "unfavorable" equilibrium (concave upwards). Frequently, if an application exhibits hysteresis (shown for Types IV and V), there may be an impact on kinetics and regenerability. Hysteresis occurs when desorption occurs along a different isotherm than adsorption, usually as a result of liquid filling pores in a certain way that is not followed when they are emptied.

The following paragraphs describe the isotherms and explain the terms that are listed in Table 2. Most can accept any form of concentration, C, for the fluid phase, e.g., having units of mol/m^3, lb/ft^3, etc., or a variable that is convenient, e.g., partial pressure, ppm, etc. Likewise they can fit any adsorbent loading, n^*, e.g., having units of mol/m^3, lb/ft^3, lb/100 lb, etc.. Generally, the parameters A and B are purely empirical.

Table 2. Pure Component Isotherm Equations

Name	Equation Form	K[1]	n_M[2]
a. Henry's Law:	$n^* = K\, n_M\, C$		∞
b. Langmuir:	$n^* = K\, n_M C / (1 + K\, C)$		
c. Freundlich:	$n^* = A\ C^B$	∞	∞
d. Brunauer-Emmett-Teller: ($C_r = C/C_{sat}$)	$n^* = K\, n_M C_r / ((1+(K-1)\, C_r)(1-C_r))$		
e. BDDT ($C_r = C/C_{sat}$)	$n^* = \dfrac{K\, n_M\, C_r\ (1+ m\ ((q-1)\, C_r^{\,m-1} + q\, C_r^{\,m+1} - (2q-1)\, C_r^{\,m}\ ) - C_r^{\,m}}{(\ 1-C_r\ )\ (1+ (K-1)\, C_r + K\ (\ (q-1)\, C_r^{\,m} - q\, C_r^{\,m+1}\ ))}$		
f. Dual Mode Isotherm:	$n^* = K_1\, n_M\, C / (1 + K_1\, C) + K_2\, C$	K_1+K_2	
g. Redlich-Peterson:	$n^* = K\, n_M\, C / (1 + K\, C^B)$		
h. Langmuir-Freundlich:	$n^* = A\, n_M\, C^B / (1 + A\, C^B)$	∞	
i. Sips:	$n^* = n_M\, [A\, C / (1 + A\, C)\ ]^B$	∞	
j. Toth:	$n^* = K\, C / (1 + C^B / A)^{1/B}$		$K\, A^{1/B}$
k. UNILAN:	$n^* = \dfrac{n_M}{2\, B}\ ln\dfrac{D+C\ exp(\ B\ )}{D+C\ exp(\ -B\ )}$	$\dfrac{n_M\, sinh(B)}{B\, D}$	
l. Dubinin-Radushkevich[3]:	$n^* = n_M\, exp(\ -((\ k_0\, \varepsilon\ /\beta_0\ )^2))$	0	n_M
m. Dubinin-Astakhov[3]:	$n^* = n_M\, exp(\ -((\ k_0\, \varepsilon\ /\beta_0\ )^n))$	0	n_M
n. Dubinin-Stoeckli[3]:	$n^* = n_{M1}\ exp(\ -((\ k_{01}\, \varepsilon\ /\beta_{01}\ )^2))$ $+\ n_{M2}\ exp(\ -((\ k_{02}\, \varepsilon\ /\beta_{02}\ )^2))$	0	$n_{M1}+n_{M2}$

[1] The Henry's law coefficient, K, is traditionally defined as the initial slope of "fractional coverage" (or $\theta = n^*/n_M$), versus concentration or partial pressure. That leads to awkward units. The maximum loading, n_M, must be known before doing calculations. If saturation is not observed, it is not reasonable to assume a value for n_M, so one has no choice but to plot n^* versus C, and use that slope. Despite these aggravations, we will stick with tradition.

[2] n_M corresponds to the "monolayer" loading for equations (a) through (e), while for the rest it represents a sort of "maximum" loading. Details go beyond the scope of this article.

[3] The adsorption capacity, n^*, and maximum loading, n_M, for this isotherm is expressed as the volume adsorbed per unit mass or volume of adsorbent.

The simplest equilibrium concept is that the extent of adsorption is proportional to the fluid-phase concentration, and this results in Henry's law [(a) in Table 2]. People's attitudes about all the other isotherm equations, and in particular about the inner meaning of their parameters, are summed-up by their regard for Henry's law. Purists say, "If it does not reduce to Henry's law at the limit of zero loading, it is thermodynamically inconsistent, and therefore wrong." Pragmatists say, "If it fits, use it."

The Langmuir isotherm [(b) in Table 2] accounts for surface-coverage by balancing the relative rates of uptake and release, the former being proportional to the fraction of the surface that is open, while the latter is proportional to the fraction that is covered. The equilibrium constant for those rates is K, which also is the Henry's law coefficient. When the fluid concentration is very high, a monolayer forms on the adsorbent surface, having a loading of n_M. Those two parameters help us understand the nature of adsorption (although for some isotherms, n_M does not strictly mean a monolayer). Hence, they are used directly in the equations when appropriate, or when possible, the equivalent terms are listed in Table 2.

Freundlich recognized that, when data does not fit well on linear coordinates, the next logical step is to try log-log coordinates, and that led to the isotherm [(c) in Table 2] bearing his name. It is probably the most commonly used isotherm equation, despite being "thermodynamically inconsistent."

The Brunauer-Emmett-Teller (BET) and BDDT isotherms, [(d) and (e) in Table 2], account for pore filling via multiple layers instead of just a monolayer, and they use C/C_{sat} which tends towards unity as the pores are completely filled. The BDDT isotherm includes the number of layers explicitly (m), as well as a heat of adsorption term (q). The BET isotherm is mostly used to estimate surface areas, not for process calculations.

The Dual Mode isotherm is merely a combination of Henry's law and the Langmuir isotherm. More imaginative isotherms, such as the Redlich - Peterson, Langmuir - Freundlich, Sips, and Toth [(g), (h), (i) and (j) in Table 2] versions extend the Langmuir isotherm by accounting for subtle nonlinearities, and are "power-law" forms. The last of this type, is the UNILAN isotherm (k). Its name comes from UNI for "uniform distribution" and LAN for "Langmuir local model." It has a strong theoretical basis, but is less satisfying to intuition since it is transcendental. It and a slightly different form of Toth's isotherm are used predominantly in the *Adsorption Equilibrium Data Handbook* by Valenzuela and Myers (Prentice-Hall, 1989) which contains a wealth of information regarding pure components and mixtures, gases and liquids. Speaking of sources of isotherm data, others are: *Carbon Adsorption Isotherms for Toxic Organics* by Dobbs and Cohen (EPA, 1980), and "Adsorption-Capacity Data for 283 Organic Compounds," by Yaws, Bu, and Nijhawan, which appeared in *Environmental Engineering World*, **1**, 3, 16-20 (1995).

Polanyi recognized about 60 years ago that there was an analogy between adsorption and condensation. Through the use of free energy, he arrived at a term called the *adsorption potential,* ε_i for component "i". The definition is:

$$\varepsilon_i = R\,T \ln (f_i^* / f_i) \approx R\,T \ln (p_i^* / p_i r) \approx R\,T \ln (C_i^* / C_i) \qquad (7)$$

where the pure fluid fugacity and vapor pressure are f_i* and p_i*, and the equilibrium fugacity and partial pressure are f_i and p_i, respectively, all at the temperature of interest, T. For vapors (neglecting fugacity coefficients), the adsorption potential is equivalent to the work required to compress the adsorbable component from its partial pressure to its vapor pressure. For liquids, C_i* is the solubility limit in solution and C_i is the solute concentration at equilibrium. In addition, to apply the approach to liquids requires deducting a correction factor from ε_i to account for the displaced solvent.

Dubinin and co-workers showed that a specific adsorbent adsorbs nearly equal volumes of similar compounds when their adsorption potentials are equal. They suggested a plot of volume adsorbed versus adsorption potential would produce a "characteristic curve," applicable to that group of compounds for the specific adsorbent. Most people who use this type of isotherm equation have adopted W as the symbol for loading (volume adsorbed per unit mass or volume of adsorbent), but we will retain n^*, and recognize that the units are specialized. From the measured data (moles or mass adsorbed), one calculates the volume adsorbed using V_m, the molar volume of the saturated liquid evaluated at the adsorption pressure, or evaluated at the normal boiling point, or another condition. Regardless, it should be consistent and clearly stated. It is easy, then, to extrapolate to other temperatures and other similar adsorbates for a given adsorbent. The main drawback is that the characteristic curve does not reduce to Henry's law at low coverage.

The isotherms developed by Dubinin and co-workers employ a power to which the adsorption potential is raised that indicates the prevalent type of pores. The Dubinin-Radushkevich equation [(l) in Table 2] was intended for microporous adsorbents since the exponent is 2. The Dubinin-Astakhov equation (m) allows the exponent, n, to vary, but a reasonable lower limit is unity (for macroporous adsorbents). The Dubinin-Stoeckli equation (n) allows a distribution of pore sizes, which is a feature of many modern adsorbents.

For this type of isotherm, n_0, represents the maximum loading, which correlates with pore volume among different adsorbents. The other isotherm parameters, k_0 and β_0 [no relation to the terms in eqs.(4) or (5)], represent the *characteristic parameter* of the adsorbent and an *affinity coefficient* of the compound of interest, respectively. The characteristic parameter, k_0, defines the shape of the n^* vs. ε curve. The affinity coefficient, β_0, adapts the compound of interest to the characteristic curve. It is a "fudge factor" that has been correlated to the ratio of molar volumes, parachors, or polarizabilities (via the Lorentz-Lorenz equation) of the compound of interest to that of a reference component (e.g., benzene or n-heptane). Those three methods are roughly equivalent in accuracy. The molar volume version is $\varepsilon_i = \varepsilon_{ref}\ V_i / V_{ref}$. The only controversy is whether to use the actual temperature to estimate volumes, or some other temperature such as the normal boiling point.

Before leaving the topic of isotherms, it is fair to ask rhetorical questions. For example, given a set of data, what isotherm equation(s) might fit best? And what is the impact on calculations of fixed bed adsorption? Unfortunately, neither question can be answered fully. Some hint at the answer might be found in a specific example, however. (Before delving into the example, it should be stated that the complexity of fitting nonlinear isotherms is beyond the scope of this article. Many methods exist, but at ARI we use a specialized program that fits the equations illustrated here, plus many more, and plots the results because visual cues are usually better than numerical ones.)

Thus, to illustrate the general principles of isotherm fitting, the most prevalent adsorbent/adsorbate pair in the world is fair: water vapor on silica gel, shown as symbols in Figure 4. In that same figure are the curves representing the best fits of the Langmuir, Freundlich, Redlich-Peterson and BDDT isotherms.

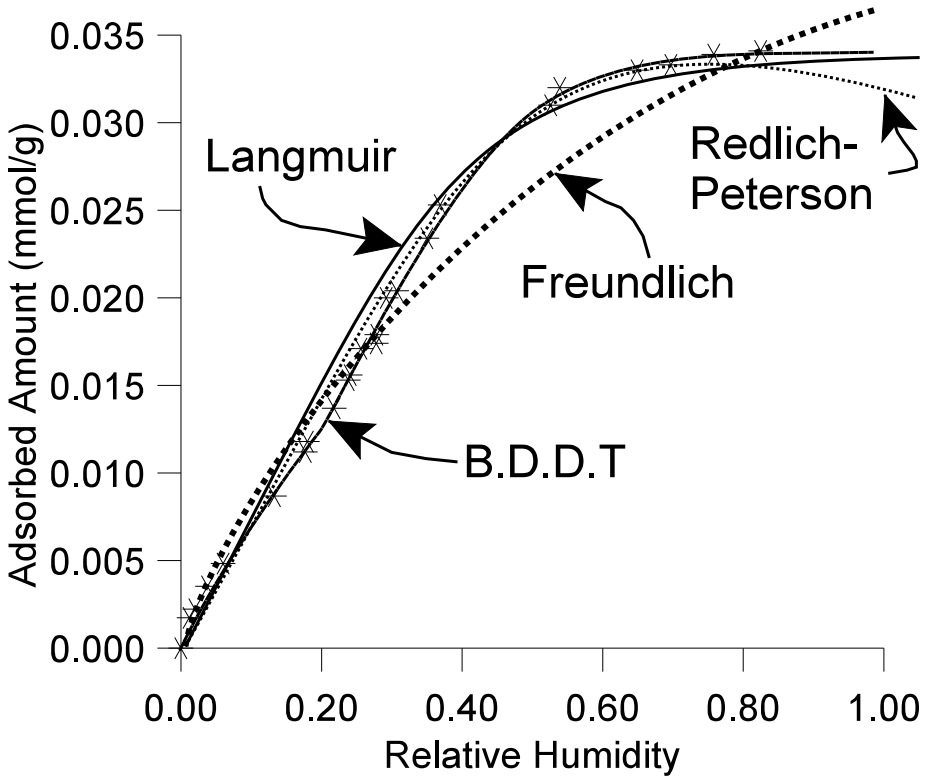

Figure 4. Isotherm Data and Fits for Moisture on Silica Gel.

The average percentage deviations for those fits are 8.8%, 12.0%, 7.9% and 2.7%, respectively. The Redlich-Peterson average error seems high due to relatively large percentage deviations for the first few points. The weighted percentage errors are 3.9%, 4.8%, 1.9% and 1%. Comments about each of these, from the best to the worst, are:

1. The BDDT isotherm essentially provides an ideal fit at low, intermediate and high concentrations. The parameters indicate that roughly 4 layers are adsorbed on the surface at saturation, and (because the others miss that, the real Henry's law coefficient is about 4 times larger than it seems).

2. The Redlich-Peterson equation fits the data pretty well, though it unforgivably predicts that loading decreases as saturation is approached. It also under-predicts the loading at low concentrations.

3. The Langmuir isotherm does pretty well at low concentrations, as far as an empirical fit goes, but it deteriorates at high concentration, near saturation.

4. The Freundlich isotherm fails in nearly every respect. If it were the only one considered, it might look OK, but it is not.

When column performance is analyzed, some engineers feel it is acceptable to use any isotherm that fits the general trend of the data. We have found, in a separate study, that sometimes the precise shape of the isotherm is important, as well as heat effects, mass transfer, and other phenomena. In fact, for the isotherm data just mentioned, only the BDDT isotherm provides reasonable predictions. Actually, the Dubinin-Stoeckli isotherm fit as well and inherently accounts for temperature effects.

3.3. Mixture Equilibria

There exist five common means of dealing with mixtures, rather than single adsorbable species. First, easiest, but sometimes disastrously wrong is to pretend that the mixture consists only of the major adsorbable component. The second approach, treating them as independent, is useful and accurate when a nonadsorbing carrier contains very dilute contaminants, and is very easy. Only pure component isotherms are required. Next is a method developed by Tien and co-workers called *species grouping*. The idea is to deal with a mixture of, say, ten components by identifying two or three (sometimes fictitious) components to represent the entire set. That reduces the complexity, saves time and money, and is fairly accurate if all that is desired is a "ballpark" answer. It requires some pure component isotherm data, in order to know how to group the species.

The fourth method is to use one of several empirical isotherm equations which account for "competitive" adsorption of the relevant components. This method requires both pure component and mixture isotherm data. Depending on which equation is selected, the data analysis and fitting are more involved than for pure components, but not enormously so. When luck prevails, the results are compact and relatively simple to use for design or simulation. Examples of the equations are listed in Table 3.

Table 3. Multicomponent Isotherm Equations

Name	Equation Form
a. Henry's Law:	$n_i^* = K_i\, n_{Mi}\, C_i$
b. Markham-Benton:	$n_i^* = K_i\, n_{Mi}\, C_i / (1 + \sum K_j\, C_j)$
c. Schay:	$n_i^* = (K_i\, n_{Mi}\, C_i / \eta_i) / [1 + \sum (K_j\, n_{Mj}\, C_j / \eta_j)]$
d. Yon-Turnock:	$n_i^* = n_{Mi} (K_i\, C_i^{A_i}) / [1 + \sum (K_j\, C_j)^{A_j}]$
e. Sips-Yu-Neretnieks:	$n_i^* = n_{Mi}\, K_i\, C_i\, (\sum K_j\, C_j)^{A_i - 1} / [1 + \sum (K_j\, C_j)]^{A_i}$
f. Redlich-Peterson-Seidel: (C_{ref}=1 [=] C_i)	$n_i^* = A_i\, C_i / [1 + B_i\, C_{ref}^{D_{ii}}\, C_i^{E_i - D_{ii}}\, \sum (A_{ij}\, C_j)^{D_{ij}}]$

Fourth, is more a field than a concise method, since it embodies so many methods, and they are all grouped together as "adsorbed mixture forms." Basically, this involves treating the adsorbed mixture (which

has a composition that can only be inferred) in the same manner as the liquid is treated when doing VLE calculations. A mixture model is used to account for interactions, which may be as simple as Raoult's law or as involved as Wilson's equation. These correspond roughly to the Ideal Adsorbed Solution and Vacancy Solution models, respectively. Pure component and mixture equilibrium data are required. The unfortunate aspect is that all versions require iterative root-finding procedures and integration. These add complexity to design or simulation routines, which may already be solving coupled partial differential equations. They may be the only route to acceptably accurate answers, however. It would be nice if adsorbents could be selected to avoid both aspects, but generally the adsorbent is only an accomplice not the cause of complexity.

3.4. Instrument Types and Data Analysis

Doing isotherm measurements is painstaking and time-consuming. It is usually even more difficult to set-up the equipment, however, than to do the experiments. Despite that, it is important to know something about how they are done, in order to discuss what they mean. There are three basic types of equipment: volumetric, gravimetric, and chromatographic. The equipment and techniques are reviewed briefly here.

The first method, volumetric, generally is a vessel containing adsorbent that is subjected to a measured step change of fluid phase concentration. The ultimate concentration reveals the amount adsorbed via a mass balance. It is easiest if there is a noninvasive way to measure concentration. For gases a pressure transducer will do, since volume and temperature are fixed. For liquids, a variety of instruments exist that can be used *in situ*, but it is also acceptable to extract small samples with a syringe for individual analysis. This method is probably the best in terms of flexibility, decent accuracy, and low cost.

Second, the gravimetric approach, mainly applies to gas-phase adsorption. It involves measuring the amount taken up by the adsorbent by weight. These isotherm measurements are quick and accurate, and the interpretation is easy. Some types of equipment are elaborate, with a small adsorbent-bearing pan suspended from a quartz spring. Then, the main problem is cost, plus the fact that the equipment tends to be finicky (each seal is subject to leaks). Other problems that are sometimes overlooked are: adsorption on the walls rather than on the adsorbent, and buoyancy effects (which can amount to more than 10% error). Another version uses a column of adsorbent, through which is passed gas of a known concentration. Periodically the flow is stopped, the column is sealed then weighed. The adsorption capacity can be determined once steady-state is reached. This is more tedious, but reliable and relatively inexpensive. Alternatively, the adsorbent can be heated strongly, and the off-gases can be trapped and analyzed to infer the adsorbate composition.

Third is chromatographic analysis. This is primarily a screening technique in which adsorbents are crushed and placed in a chromatographic column, then a pulse of the components of interest is injected into a nonadsorbing carrier fluid. In principle, the technique applies to both gases and liquids, but the former is much more popular. The Henry's law coefficient can be determined readily from the retention of each peak.

3.5. Adsorption Dynamics

In order to select an adsorbent, one must appreciate the impact of processing conditions on performance. This does not mean becoming familiar with methods to solve the governing partial differential equations. It just means that awareness of the variables and parameters involved in transport phenomena, beyond their definitions, can help when picking an adsorbent. As potentially complicated as that might sound, there are really only three topics that are important in most cases: intraparticle diffusion, interstitial mass transfer, and packed bed flow behavior. Although each of these has been the topic of dozens of technical papers, there are some very simple generalizations that are sufficient to cover most situations.

First of all, intraparticle diffusion is characterized by an effective diffusivity, $D_{eff}=D_{AB}\,\varepsilon_P/\tau$ (where D_{AB}

is the solute diffusivity in the fluid, ϵ_P is the particle void fraction, and τ is its tortuousity), and for a sphere or cylinder the particle radius (or microcrystal radius), ℓ (for a sphere or cylinder shape), and time, t. The relevant grouping is: $D_{eff}\, t/\ell^2$. For example, the initial response ($D_{eff}\, t/\ell^2 < 0.4$), and final response ($D_{eff}\, t/\ell > 0.4$) of a spherical particle to a sudden change of composition, respectively, are approximated by

$$F \equiv \frac{C_t - C_0}{C_f - C_0} \approx \frac{6}{\sqrt{\pi}} \left(\frac{D_{eff}\, t}{\ell^2} \right)^{1/2} - 3\, \frac{D_{eff}\, t}{\ell^2} \approx 1 - \frac{6}{\pi^2}\, e^{-\pi^2 D_{eff}\, t / \ell^2} \qquad (8)$$

where the C_0, C_f, and C_t represent the initial, final and instantaneous values of concentration averaged over the particle. From these approximations we can see that when $D_{eff}\, t/\ell$ is less than 0.001, not much has happened within the particle. Conversely, when it exceeds unity, what was going to happen is largely complete. Thus, when searching for an effective (fast) adsorbent, it is usually a safe bet to choose one having a large diffusivity or small diameter. Other concerns may overrule the selection of small particles, as mentioned later.

4. Adsorbent Selection Criteria: Case Studies

We have reviewed the performance criteria, basic properties, and governing equations involved in adsorbent selection. Now, the sole remaining obligation is to answer the question, "how are these actually used?" That is easier said than done, since every application is different. By breaking the field into discrete parts, at least some generalizations can be made. We will focus on the criteria stated at the beginning: ***capacity***, ***selectivity***, ***regenerability***, ***kinetics***, ***compatibility***, and ***cost***.

4.1. Ordinary Adsorption

This topic covers situations in which adsorption has "always" been used, for which no other unit operation is deemed suitable, or for which adsorption is the last resort. Examples are water or air purification of every sort, and clean-up of odoriferous or noxious contaminants. Typically, one would buy adsorbent, or in some cases a modular, pre-filled adsorber and install it. Assuming it solves the problem, it is forgotten until the problem is noticed again or until a certain amount of time elapses, when it is replaced.

1. dilute gaseous emissions

Let's take as our first example a process vent containing, say, 100 ppm (vol.) each of MEK, n-hexane, and toluene, at a flow rate of 1 to 10 cfm, and at 80°F. One immediately thinks of activated carbon, with one reservation: compatibility. Ketones in particular have been notorious for causing bed fires in activated carbon systems. Though some new activated carbons are resistant to spontaneous ignition, it is still a good idea to plan for Murphy's law. Thus, even at this seemingly low concentration and flow rate, it would be prudent to install a deluge system to be interfaced with a CO monitor at the downstream end of the unit. To avoid that complication, other adsorbents might justify consideration, because they are much less likely to spontaneously ignite. Two types are polymeric adsorbents and silicalite. Due to space, we will go on the assumption that activated carbon is acceptable, and it is certainly the least expensive on a single-use basis.

To estimate capacity, vendors can be contacted, you might use a database, you might arrange to conduct the measurements, or you might arrange to have tests conducted by an independent firm. At ARI we have an extensive database that is useful for rough estimates of this sort. In Table 4 are some loadings from that source, based on one coal-based ("A") and one coconut shell-based ("B") activated carbon. There is a cost differential of 1.5 for carbon "B" over carbon "A." Taking a closer look at the loadings, it is easy to see why

the cost is so much higher for "B": basically you get what you pay for.

Multicomponent adsorption is complex, as alluded to before. Since this is a small application, delving into equilibria and column modeling is not justified. We can instead assume that the lighter components are displaced by the heavier components. The flow rate, up to 10 cfm at 80°F, amounts to 9.1 scfm or 1.52 lbmol/hr. From that we can estimate the time "on-line" provided by either adsorbent for each compound, assuming that they adsorb independently, and completely (no premature breakthrough). The best choice appears to be carbon "B," since it offers a longer time on-line than carbon "A" for the critical component, MEK, and the ratio is greater than the cost differential.

Table 4. Estimated loadings and service times of emitted components (at 100 ppm each) for activated carbons "A" and "B" at 80°F.

Component Name	Loading (lb/100 lb)		Loading	Mol.Wt.	Max. On-Line (hr/100 lb)	
	Carbon "A"	Carbon "B"	"B"/"A"	(g/mol)	"A"	"B"
Methyl Ethyl Ketone	7.5	13.2	1.76	72.10	683	1203
Toluene	19.6	28.8	1.47	92.14	1398	2054
n-Hexane	12.3	19.1	1.55	86.18	938	1456

The final consideration is the type and cost of equipment. Modular units come packed with 150 to 500 lb of carbon. These can be installed and removed quickly, and returned to the manufacturer on an exchange basis (possibly avoiding "hazardous waste" aspects). One of the smaller units could be packed with 4x6 mesh carbon, and could handle up to 100 cfm. Furthermore, it could be viewed as having 50 lb allotments per contaminant. According to Table 4, there would be some safety factor for an "on-line" time of 600 hr, but not much. Depending on the vendor, the cost per drum would be in the range of $600. Even at this low a cost, it might be possible to justify a small PSA unit that would recover concentrated vapor (for incineration), or a condensed product. Such systems are not yet available "off-the-shelf," however.

2. dilute aqueous emissions

An analogous situation exists when a noxious or valuable contaminant is present in water. Examples are: the silver-laden waste from photographic developing that used to be discarded, or well-water containing sulfur or iron, or dozens of wastewater applications. For example, a difficult application is removal of halogenated phenolics from wastewater. The equilibration time for activated carbon is long, which means that the diffusivity is low, and that the breakthrough curve could be very distended. Let's look at a specific case, say, 1 mg/l (or 1000 ppm) of 2-chlorophenol in 100 gpm water, with a minimum "on-line" time of 500 hr. The report by Dobbs and Cohen that was mentioned earlier indicates that Filtrasorb-300 (Calgon Corp.) adsorbs 57.1 mg/g at this concentration. They also noted that a fine powder (200x400 mesh, or 0.05 mm diameter) required about 2 hr to equilibrate. Equation (8) gives us an idea of how long a 2 mm diameter granule might take. Namely, the parameter $D_{eff}\, t/\ell^2$ would be constant, as would the effective diffusivity. Thus, $t_{3\,mm} = t_{0.05\,mm}$ (3 mm /0.05 mm)^2 or 300 days! This material cannot be expected to exhibit a step change upon breakthrough. Therefore, a large safety factor is essential. It is also a valid reason for using a slurry of carbon in the powdered form, even though a downstream filter is required to recover the waste.

Equation (16) can be used to estimate the equilibrium breakthrough time. Let's use a bulk density of 31.2 lb/ft^3 (or 0.5 g/cm^3) and a porosity of 70%. From the data above, we find:$\Delta q/\Delta C$=57.1 (mg/g)/0.001 (mg/cm^3). Thus, the minimum volume of adsorbent is: 14. ft^3 or roughly 440 lb. To be conservative, a factor of 3 is recommended, but frankly given these kinetics, even that should be tested. Thus, the bed size would be about 50 ft^3, containing about 1600 lb of carbon. The remaining decision is the length-to-diameter ratio. To obtain a large mass transfer coefficient, that ratio should be large, but to minimize pressure drop, that ratio should be small.

4.2. Pressure or Temperature Swing Adsorption

The sophistication required for designing a PSA system or TSA system is much greater than for a simple adsorber. So much so, that even using simple rules-of-thumb would be beyond the scope of this article. Regardless, two rules-of-thumb are: that selectivity is much more important than capacity, and that regenerability is even more important. Instead of pursuing concepts such as those, it might be useful to consider a few situations, and the relevant criteria for making an adsorbent selection. To keep the discussion as simple as possible, all details except those essential the point have been omitted.

For example, a PSA application came up for which several similar adsorbents could be used. We investigated them and found the results listed in Table 5. The selectivity mentioned is the one defined in eq. (3). Likewise the effective diffusivity is the same one as discussed in eq. (8). The first point to notice is that Adsorbent 1 is superior in two respects: it is the *fastest* and it is the *least expensive*. Because its selectivity is low, in fact, more than a factor of four lower than that of Adsorbent 5, its economy might be an illusion. In particular, the vessel containing that adsorbent would be perhaps three- or four-times larger, to compensate for the lower selectivity, than if filled with Adsorbent 5. Furthermore, without doing bench-scale testing at the very least, it is impossible to know whether the differences in effective diffusivities will significantly affect performance. Other factors not yet taken into account here are: particle size, pressure drop, vendor reliability, and compatibility (e.g., sensitivity to contaminants in the feed).

Table 5. Comparison of Five Candidate Adsorbents for a PSA Application : Selectivity & Diffusivity×Absolute Pressure for Relevant Gases (A+B)

ADSORBENT	α_{AB}	$D_{Aeff} \times P$ ($\times 10^{-8}$ cm^2 atm)		Cost
	K_A / K_B	A	B	$/lb
Adsorbent 1	1.56	16130	29870	0.50
Adsorbent 2	3.40	113	223	1.10
Adsorbent 3	4.67	205	603	0.89
Adsorbent 4	6.65	3610	1059	1.27
Adsorbent 5	7.57	9338	19600	1.65

5. Conclusions

In this article many subjects have been covered. Among the most important are the general criteria for selecting an adsorbent: capacity, selectivity, regenerability, kinetics, compatibility, and cost. Specific details regarding adsorbents were also covered, including appearance, structure, effective surface area, required pretreatment, physical forms, manufacturers, and applications. The materials covered included inorganic materials (such as aluminas, silicas, and zeolites), and organic materials (such as carbons and polymers). The criteria for choosing adsorbents were explained, and included adsorption equilibrium, isotherm equations, mixture equilibria, instrument types and data analysis, and adsorption dynamics. Finally, a few case studies were mentioned briefly.

The major points to keep in mind are that there are dozens if not hundreds of options among adsorbent types and manufacturers. New varieties are being introduced constantly. The nature of competition is such that, generally, not a word is whispered about those under development until they are ready to be sold. So relying on a historical product line is not necessarily prudent, unless the application is very ordinary. On the other hand, even though new products may appear "optimal" due to forceful sales presentations, they may not be best for your particular application. It is best to approach the task by asking the right questions to get to the bottom of which material best satisfies all the criteria, and not being satisfied with jargon for answers.