

CHAPTER II

HISTORICAL BACKGROUND

2.1 Activated Carbon

The two principal physical features of activated carbon, upon which its properties of commercial value depend, are surface and pore structure. The role that surface plays can only be understood in relation to the phenomenon of adsorption.

Adsorption is usually explained in terms of the surface tension (or energy per unit area) of the solid. Molecules in the interior of any solid are subjected to equal forces in all directions, whereas molecules in the surface are subjected to unbalanced forces. The resulting inward forces can only be satisfied if other molecules, usually gaseous or liquid, become attached to the surface. The attractive forces are the same as those responsible for surface tension and condensation in liquids. They are relatively weak and are called Van Der Waal's forces. When such forces are involved, the adsorption is termed "physical", and the adsorbed molecules are easily released from the surface, i.e., "desorbed". In contrast to this, chemisorption is the result of chemical interaction with surface molecules. Stronger forces are involved, and the process is irreversible; that is, the molecules originally adsorbed are recovered in the form of compounds containing atoms of the adsorbent. Both physical and chemisorption are included in the general term "sorption".

There is at present no known method of measuring the surface tension of a solid directly. However, the total surface energy is equal to the

product of the surface energy per unit area and the total surface area. For this reason, high surface area is the prime consideration in adsorption; and activated carbon usually have surface areas in the order of 500-1400 square meters per gram.

2.2 Surfactant

Surface-active agents, or surfactants, are specialty chemicals frequently used by the chemical process industries(CPI). However, many engineers do not have a comprehensive understanding of the role of surface phenomena and chemistry governing them.

Surfactant have a characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a *lyophobic group*, together with a group that has strong attraction for the solvent, called the *lyophilic group*. This is known as an *amphipathic* structure. When a surface-active agent is dissolved in a solvent, the presence of the lyophobic group in the interior of the solvent may cause distortion of the solvent liquid structure, increasing the free energy of the system. In an aqueous solution of a surfactant this distortion of the water by the lyophobic (hydrophobic) group of surfactant, and the resulting increase in the free energy of the system when it is dissolved, means that less work is needed to bring a surfactant molecule than a water molecule to the surface. The surfactant therefore concentrates at the surface. Since less work is now needed to bring molecules to the surface, the presence of the surfactant decreases the work needed to create unit area of surface (the surface free energy per unit area, or surface tension). On the other hand, the presence of the lyophilic (hydrophilic) group prevents the surfactant from being expelled completely from the solvent as a separate phase, since that would require dehydration of the hydrophilic

group. The amphipatic structure of the surfactant therefore causes not only concentration of the surfactant at the surface and reduction of the surface tension of the water, but also orientation of the molecule at the surface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it.

2.3 Adsorption

Adsorption is a process where molecules from the gas phase or from solution bind in a condensed layer on a solid or liquid surface. The molecules that bind to the surface are called the **adsorbate** while the substance that holds the adsorbate is called **adsorbent**. The process when the molecules bind is called **adsorption**. Removal of the molecules from the surface is called **desorption** (Richard I. Masel, 1996).

The nature of bonding between adsorbates and surfaces is still subject to some interpretation. Taylor (1931) suggested that it was important to distinguish between two radically different types of adsorption: **Chemisorption**, where there is a direct chemical bond between the adsorbate and the surface, and **Physisorption**, where there is no direct bond. Instead the adsorbate is held by physical (i.e., van der Waals) forces. On a more fundamental level, when a molecule is chemisorbed, the electrons are shared between the adsorbate and surface. As a result, the adsorbate's electronic structure is significantly perturbed. The surface's electronic structure is perturbed to a lesser extent. In contrast, physisorption is governed by polarization (i.e., van der Waals) forces. The surface does not share electrons with the adsorbate. As a result, the electronic structure of the adsorbate is perturbed to a much lesser extent. Therefore, a more direct test of whether a molecule is physisorbed or chemisorbed is:

A molecule is **physisorbed** if it adsorbs without undergoing a significant change in electronic structure.

A molecule is **chemisorbed** if the molecule's electronic structure is significantly perturbed upon adsorption.

Typical chemisorption energy are 15-100 kcal/mole for simple molecules. That compares to 2-10 kcal/mole for physisorption.

2.3.1 Physical Adsorption Methods

The most important methods for specific surface area analysis of solids are based on adsorption. The following two assumptions are made:

1. It is possible to determine the quantity of adsorbate required for complete coverage of the substrate surface by a monolayer.
2. The cross-sectional area of an adsorbed molecule is known and independent of the substrate (adsorbent).

Strictly speaking, these two requirements contradict each other on physical grounds: in the case of strong interactions of the substrate with the adsorbate we obtain an isotherm with a pronounced plateau at complete coverage with a monolayer; the effective area of an adsorbate molecule, however, depends on the atomic structure of the surface. In the case of weak interactions between substrated surface and adsorbate where the interaction energy is comparable with the interaction between adsorbate molecules themselves, multilayer adsorption is obtained before the monolayer is complete. The isotherm does not have a distinct plateau, and the monolayer has to be calculated from the isotherm on the basis of model concepts. Still, numerous investigations have shown that the measurement of physisorption isotherms is the most reliable method, although the theoretical basis of model concepts is still unsatisfactory (Raouf Sh. Mikhail, Erich Robens, 1983)

When a molecule is physi- or chemisorbed on the surface of a solid, the molecular electrons interact with those determining the surface state of the solid. Physisorption is the binding with correlated motion of the electrons in these respective states. The sorption heat released is of the order of the heat of condensation of the adsorbed gas. Physisorption is a reversible process in so far as the adsorbate can be almost completely removed by application of a vacuum. Chemisorption, on the other hand, depends on overlap between the electron distribution of surface molecules and that of adsorbed molecules, including electron exchange. The overlap and exchange interactions produce a stabilization. The chemisorption heat released is of the order of chemical reaction energy. Chemisorption is a distinctly activated process; desorption requires the supply of heat or energy.

The transition between the two types of binding is not sharp, however, and it is even further blurred by the heterogeneity of real surfaces. In fact, the desorption of a physisorbed layer is more or less an activated process. The frequently quoted upper limit of 40 kJ/mol for the physisorption heat, therefore can be regarded only as an approximate value.

2.3.2 Nonporous Solids

Henry's law region

According to Henry's law the amount adsorbed V_a in cm^3 per gram sample mass is related to the pressure p and the area S by the following equation

$$V_a = 10^{-3} k_H p S \quad (2.1)$$

if p is in bar, S in square metres per gram, and k_H in nanometers per bar. The Henry's law constant k_H can be regarded as the equivalent penetration into the

solid of gas at 1 bar. Since the adsorption of gases on the majority of adsorbents conforms to Henry's law at low coverate ($p/p_0 < 0.01$), the surface area can be calculated from a single adsorption point in the low coverate region. Since most adsorption equations also conform to Henry's law at very low surface coverage, Innes related Henry's law constant k_H to the constants of the other adsorption equations as follows:

$$k_H = V_m C \times 10^3 / p_0 \quad (2.2)$$

where V_m and C are the BET equation constants,

$$k_H = V_L a \times 10^3 / S \quad (2.3)$$

where V_L and a are the Langmuir equation constants.

V_L is the volume of the monolayer in cm^3/g computed by the Langmuir equation.

a is the isothermal adsorption constant for the Langmuir equation (bar^{-1}).

$$k_H = V_b \times 10^3 / KS \quad (2.4)$$

where V_b is the volume of the monolayer in cm^3/g computed by van der Waals' equation

K is the isothermal constant for the adsorption equation corresponding to the van der Waals' equation (bar).

The temperature coefficient of k_H is only modified slightly by a nonuniform surface at elevated temperature, that is, by the second term in the equation.

2.4 Carbon as Adsorbents

Active carbon is probably the oldest adsorbent known (J.C.P. Broekhoff and B.G.Linsen, 1970). In fact, wood charcoal might have been the first “chemical product” made by man, since it would no doubt have been produced with the first artificial fire.

It is well known that the van der Waals forces are responsible for the adsorption on carbon in most of the applications where adsorption from gaseous mixtures is practiced. The adsorption from liquids may be different and will be considered in more detail later on.

The adsorption process as such is, therefore, not very selective as far as the adsorption forces are concerned. This might be influenced if the texture of the carbons could be controlled in such a way that appreciable molecules sieve action occurs.

The main advantage of carbons in adsorption processes seems to be the large surface area they offer at a relatively low price. Especially in the case of adsorption from gases, where narrow pores are effective, the specific surface area of carbons produced for this purpose can be enormous (of the order of $1000 \text{ m}^2/\text{g}$). In addition, narrow pores give rise to an increased adsorption energy (de Boer and Custers, 1934). Carbons used for adsorption from gases generally are manufactured in the form of particles with dimensions of the order of several millimetres and irregular shape.

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generally are manufactured in the form of particles with dimensions of the order of several millimetres and irregular shape.

Carbons used for adsorption from liquids are produced as fine powders for easy suspension. The ideal pore size for this type of application is larger than for use with gases, since the slower diffusion of dissolved products in the liquid phase must be compensated for by larger pores. The extremely fine pores, useful for adsorption from gases, are not desirable in the case of liquids.

Apart from the pore sizes there is the requirement of easy dispersion of the carbon in the liquid to be treated. A surface consisting of carbon only, or carbon plus hydrogen, would be strongly hydrophobic and not at all suited for the treatment of water. The presence of oxygen on the surface tends to make it more hydrophilic and does not influence the adsorption properties adversely. The oxygen can be fixed on the carbon by a mild oxidative treatment; most of the activation processes in common use introduce fixed oxygen together with the porosity produced by the removal of carbon as CO_2 or CO .

The more polar character of the surface, arising from the partial coverage with oxygen, influences the adsorption properties in the direction of an increased adsorption of polar substances.

A special case is the adsorption of electrolytes on carbon that contains oxygen. Depending on the oxidizing treatment, two forms of carbon can be produced, one that assumes a positive charge in water or one that becomes negatively charged. The charge on the solid is, in either case, compensated by the charge of a mobile double layer, in which an excess of ions of a sign opposite to that of the carbon surface is present.

The adsorption of electrolytes such as potassium chloride, etc., can be described as an exchange of ions with the original components of the double layer. Ions of larger molecular weight, such as organic acids or bases, are adsorbed irrespective of the sign of the large ion. Here the influence of the van

der Waals forces predominates; the large ions are adsorbed on the carbon surface and do not form a part of the double layer. If the sign of the charge on the large ion is not the same as that of the carbon surface, an apparent reversal of the charge on the solid may be noted.

From the above considerations it would follow that the behavior of a certain carbon product is determined by:

- (a) its texture: specific surface area, pore shape and pore size distribution;
- (b) the coverage of the surface with oxygen;
- (c) the chemical form assumed by the oxygen attached to the carbon;
- (d) the particle size distribution.

In a number of applications the carbon is impregnated with substances in order to improve its capacity and, especially, its selectivity. In most of these applications the carbon seems to function as an inert carrier, giving the possibility of obtaining, for a given mass of impregnant, a much larger active surface area than could be reached with the pure impregnant. Here, of course, the texture of the original and of the impregnated carbon are of importance. They may in fact be significantly different, e.g. because of a blocking of small pores by the impregnant.

It follows, then, that a carbon adsorbent can be characterized by the quantities referred to under a-d above. Methods of determining these quantities should, therefore, be available. The following sections deal mainly with these problems.

Another topic of great interest, the preparation of carbons to suit a given application, will not be discussed at all. Here, practical experience has had a great advance on scientific insight and the more refined methods of measurement have served mainly to confirm old ideas.

This does not mean that no progress is possible in tailoring carbons for specific purposes. Numerous studies give insight into the relationships between the properties of final products and the properties of raw materials and the parameters of the activation processes.

In the previous discussion the expression “ carbons ” has been used in a very wide sense, equivalent to that of using the word “ steel ” when discussing the structural properties of ferrous alloys. Both words indicate a large family of materials, with different properties and different applications.

In what follows, the carbons to be discussed (mostly carbon blacks) have been indicated by their trade names where possible. Since these products are manufactured with good reproducibility, this seems to make sense since a comparison of different batches of these products has been proven to be fully justified. A comparison with literature data is thereby made possible.

2.5 Previous Work

In previous SECR, Blakeburn and Scamehorn (1989) studied in a liquid phase application and found that the activated carbon can be regenerated by using the regenerant solution which contains cationic surfactant in a reasonable volume. Tert-butylphenol can be removed by 80%, a heel of adsorbed solute is very difficult to remove which comes from the chemisorbed solute. Most of the residual surfactant can be easily removed by a water flush, but large volumes of water are needed for nearly complete removal of surfactant from the carbon.

In another SECR process in liquid phase application, Bhummasobhana et al. (1996), also studied the effect of regeneration and flushing conditions on effective adsorption capacity upon repeated usage and on the breakthrough curve of the solute (phenol) in subsequent adsorption cycles. This study showed that greater pore volumes of regenerant, and greater pore volumes of water

flush solution are used, reduction of the effective carbon adsorption capacity decrease with higher regenerant concentration of surfactant. Bhummasobhana et al. also studied the activated carbon regenerated by the SECR in liquid phase application can be effective in subsequent adsorptions.

In a previous study of the use of SECR to treat activated carbon used in a vapor phase application, Roberts et al. (1989), studied the application of SECR process to regenerate carbon containing either toluene or amyl acetate. Using SDS, the regeneration step and water flushing to remove residual surfactant was effective, in this case little reduction in adsorption capacity of the regenerated carbon was observed after regeneration.

In another SECR process in vapor phase application, Sutad na Ayoothaya et al. (1996), showed that as the flow rate of regenerant solution is increased, the effective capacity of the regenerated carbon increases and the trichloroethylene exhibits a significant mass transfer limitation during regeneration.

These previous studies have demonstrated the general features of SECR in liquid and vapor phase applications. The purpose of this study is to measure breakthrough curves for the adsorption of model organic solute (trichloroethylene) from air in an adsorption cycle following a regeneration/flush process under varying condition. The effect of amount of flushing water in flushing step on the effective adsorption capacity with repeated usage is the variable of interest.