CHAPTER III

THEORY

3.1 Activated Carbon

Activated carbon is a processed carbon material with a highly developed porous structure and a large internal specific surface area, and it is capable of collecting gases, liquids, or dissolved species on the surface of its pores. Compared with other commercial adsorbents, activated carbon has a broad spectrum of adsorptive activity, excellent physical and chemical stability, and ease of production from waste materials.

Figures 3.1.1-3.1.2 illustrate the structures of graphite and turbostratic carbon, respectively. Activated carbon is similar to the latter type, having microcrystallites only a few layers in thickness and less than 10 nm in width. The level of structural imperfections in activated carbon microcrystallites is very high, which results in many possibilities for reactions of the edge carbons with their surroundings.

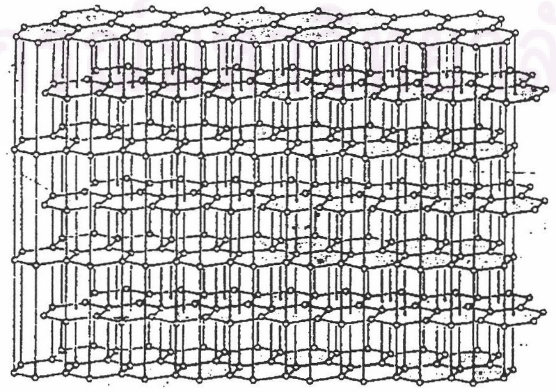

Figure 3.1.1 Graphite Lattice

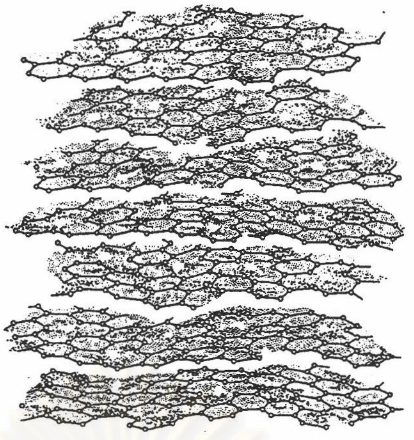

Figure 3.1.2 Turbostratic Structure

3.1.1 Production of activated carbon

Almost any carbonaceous raw materials can be used for the manufacture of activated carbon. Source materials that have been studied for the production of activated carbon are following:

Bagasse	Carbohydrates	Cereals	Coal
Coconut shells	Coffee beans	Corncobs	Cottonseed hulls
Fruit pits	Graphite	Lignin	Lignite
Molasses	Nut shells	Peat	Petroleum coke
Rice hulls	Rubber waste	Sawdust	Wood

The activated carbon can be produced in one of two ways:

- By carbonizing material with the addition of activating agent such as $ZnCl_2$, $CaCl_2$, and H_3PO_4 which influences the course of pyrolysis. This method is generally called as "chemical activation".
- By carbonizing raw material and then reacting with suitable gaseous substances (steam, carbon dioxide, or oxygen). This method is generally known as "physical activation".

Chemical activation

In chemical activation process the starting material is mixed with chemicals, and then kneaded, carbonized and washed to produce the final activated carbon. The most widely used activation agents are

Aluminum chloride	Ammonium chloride	Boric acid
Calcium chloride	Calcium hydroxide	Hydrogen chloride
Iron salt	Nickel salt	Nitric acid
Phosphoric acid	Potassium hydroxide	Potassium sulfide
Potassium permanganate	Sodium hydroxide	Sodium oxide
Sulfuric acid	Sulfur dioxide	Zinc chloride

The chemicals incorporated to the interior of precursor particles react to form products resulting from the thermal decomposition of the precursor, reducing the evolution of volatile matter and inhibiting the shrinkage of the particle. In this way, the conversion of the precursor to carbon is high, and once the chemicals are eliminated after the heat treatment, there is the porous product. Chemical activation offers several advantages: (1) it is performed in one stage that consists of carbonization and activation, (2) it yields higher carbon products, (3) it uses lower temperature, and (4) in most cases part of the added chemicals are easily recovered. However, chemical activation involves hazardous chemicals and the recovery of these chemicals from the products or off gas results in multiple operations. Non-recovery of chemicals not only makes the process uneconomical but also contributes to environmental pollution.

Chemical activation is usually carried out at temperatures from 400-800^{O}C. The variables that have influences in the development of porosity are the degree of impregnation that is the weight ratio of the anhydrous activation salt, starting material, and the temperature of activation. The chemicals are introduced into the precursor, to produce physical and chemical changes, modifying the thermal degradation process. As a consequence, the temperature of the process does not need to be high.

During impregnation and especially during evaporation there are a weakening of the precursor structure, a hydrolysis reaction, an increase in elasticity, and swelling of the particles. For small degree of impregnation, the increase in the total pore volume of the product with increase in the degree of impregnation is due to the increase in the number of small pores. When the degree of impregnation is further raised, the number of larger-diameter pores increases and the volume of the smallest decreases. After carbonization, most of the chemical is still in the particle, and the intense washing to eliminate it produces the porosity. This means that the amount and distribution of the chemical incorporated in the precursor govern the porosity of the carbon, thus making this activation very flexible for the production of activated carbon with different pore size distributions.

Physical activation

Carbonization

Carbonization is one of the most important steps in the production process of activated carbons since it is in this course which the initial porous structure is formed. During carbonization most of the non-carbon elements, hydrogen and oxygen are first removed in gaseous form by thermal decomposition of the starting material, and the freed atoms of elementary carbon are grouped into organized crystallographic formations known as elementary graphitic crystallites. The mutual arrangement of the crystallites is irregular.

The important parameters that determine the quality and the yield of the carbonized product are the rate of heating, the final temperature, the soaking time at the final temperature, and the nature of the raw material.

The final temperature is the most important parameter in the process; this is associated with the amounts of energy needed to split of the weaker chemical bonds and to enable migration of the volatile products of thermal decomposition of the raw material to the granule or grain environment. As the carbonization temperature is increased, the condensation processes in the material are enhanced and the greater the mechanical strength of the resulting granules becomes.

The soaking time of the carbonaceous material at the final carbonization temperature has an effect on the ordering of the compact structure of the carbon material. We distinguish here two principal temperatures at which the effect of time is different:

1. A temperature lower than that at which the main thermal decomposition reactions appropriate to the given raw material are terminated.

2. A temperature higher than that of the internal transformations at which the final porous structure of the carbonizate is established.

In the first case, a further slow thermal decomposition of the carbon material continues over time. However, some part of the decomposition processes has become inhibited. The carbonizate shows a greater reactivity towards the activating agents than that in which the reactions of the volatile pyrolysis products between each other and the carbon material, and the generation of carbon crystallites have been brought to an end.

In the second case, i.e. at a temperature higher than at which the main thermal decomposition processes are terminated, with elapse of time a further ordering of the internal structure of the carbon material proceeds with the possible generation of crystallites. As carbonization continues, the volume of the smallest pores usually decreases due to the further decrease of the volume of the carbonized mass. Therefore, the reactivity of the carbonizate obtained becomes lower the longer it is maintained at the final carbonization temperature.

The next important parameter of the carbonization process is the heating rate at which the final temperature is achieved. When the temperature is raised rapidly, the particular stages of the thermal decomposition of coal and the secondary reactions of the pyrolysis products with each other overlap, so control of the establishment of the porous structure in the carbonizate is more difficult. If the temperature is raised rapidly, a large quantity of volatile matter evolves within a short time, and as a result pores of greater sizes are usually formed. The reactivity of the carbonizate obtained in this way is greater than that of the products heated at a slow rate. This is due to the greater porosity and reduced ordering of the compact carbon material as compared with carbonizates obtained from the same raw material but at a low rate of heating.

The thermal decomposition of carbonaceous material, the course of the secondary mutual reactions of the pyrolysis products and the reactions of the latter with the solid carbonizate are also affected by the atmosphere in which the carbonization process is conducted. If the gases and vapors evolving during pyrolysis are rapidly removed by a neutral gas or combustion gases, then the quantity of the carbonizate obtained is smaller but its reactivity is greater.

The main aim of the carbonization process is to generate in the granules and grains the required porosity and ordering of structure of the compact carbon material. Both these factors have a crucial effect on the reactivity of the carbonizate in its reaction with the gaseous activating agent. This reactivity increases (1) with the degree of porosity generated and (2) with reduction in the ordering of the compact carbon matter. A large volume of pores in the carbonizate facilitates the diffusion of the gaseous activator into the granules and ensures a large surface area on which chemical reactions may take place.

Activation

The oxidizing agents most often used are steam, carbon dioxide, oxygen (air). During the activation of the carbonized product, first the disorganized carbon is removed, and the surface of the carbon crystallites becomes exposed to the action of the oxidizing agent. Details of the mechanism of this process, however, are not yet reliably understood.

The removal of unorganized carbon and the non-uniform burnout of elementary crystallites lead in the first phase of activation to the formation of new pores and the development of the microporous structure. In the subsequent phases, however, the effect that becomes increasingly significant is the widening of existing pores or the formation of larger size pores by the complete burnout of walls between adjacent micropores. This leads to an increase in the volume of transitional and macropores, whereas the volume of micropores diminishes. As a measure of the degree of activation the so-called burn-off is usually used, which is the percentage weight decrease of the material during activation, compared to the original carbonized product. Sometimes the so-called activation yield is used, which is the weight of the resulting activated carbon expressed as a percentage of the carbonized intermediate product prior to activation. The burn-off (B) and the activation yield (A) are related thus:

$$B = 100 - A$$

The carbon atoms, which form the structure of the carbonized product, differ markedly from one another in their affinity towards the activation agent. Those at the edges and corners of elementary crystallites, and those situated at defective places of the crystal lattice, are more reactive, because their valencies are incompletely saturated by interaction with neighboring carbon atoms. These places are the so called "active sites" on which reaction with the activation agent occurs; these sites represent only a small part, at the most only a few percent of the total surface exposed to the reaction. In the reaction of a gaseous activation agent with carbon, complex surface compounds are temporarily formed on the active sites, and on their decomposition the oxidized carbon is removed from the surface as gaseous oxides (carbon monoxide or dioxide). As a result of this, new incompletely saturated carbon atoms become exposed on the surface of the crystallites and the active sites are thus again prepared to react with further molecules of the activation agent. Details of the mechanism by which carbon reacts with steam, carbon dioxide and oxygen are shown below:

- **Activation with steam**

The reaction of steam with carbon is endothermic and a stoichiometric equation has the form:

$$C + H_2O \rightarrow H_2 + CO \qquad \Delta H = +130 \text{ kJ/mol}$$

The rate of gasification of carbon by a mixture of steam and hydrogen is given by the formula:

$$\nu = \frac{k_1 P_{H2O}}{1 + k_2 P_{H2O} + k_3 P_{H2}} \quad \text{..........(1)}$$

where: P_{H2O} and P_{H2} are the partial pressures of steam and hydrogen, respectively, k_1, k_2, k_3 are the experimentally determined rate constants. The following reaction scheme is accepted as highly probable:

$$C + H_2O \leftrightarrow C(H_2O)$$
$$C(H_2O) \rightarrow H_2 + C(O)$$
$$C(O) \rightarrow CO$$

The inhibiting effect of hydrogen can be ascribed to its occupying active centers on which it becomes absorbed:

$$C + H_2 \leftrightarrow C(H_2)$$

It was assumed that the first step of the reaction is the dissociated adsorption of water molecules according to the scheme:

$$2C + H_2O \rightarrow C(H) + C(OH)$$
$$C(H) + C(OH) \rightarrow C(H_2) + C(O)$$

Hydrogen and oxygen are adsorbed at neighboring active sites, which account for about 2 percent of the surface area.

The reaction of steam with carbon is accompanied by the secondary reaction of water-gas formation, which is catalyzed by the carbon surface:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -42 \text{ kJ/mol}$$

Activation with steam is carried out at temperatures from 750 to 950^{O}C with the exclusion of oxygen, which at these temperatures aggressively attacks carbon and decreases the yield by surface burn-off. It is catalyzed by the oxides and carbonates of alkali metals, iron, copper and other metals; the activation catalysts usually employed in practice are carbonates of alkali metals, which are added in small amounts to the material to be activated.

- **Activation with Carbon Dioxide**

For the rate of gasification of carbon by carbon dioxide an equation analogous to that for the reaction with steam has been derived:

$$v = \frac{k_1 P_{CO2}}{1 + k_2 P_{CO} + k_3 P_{CO2}} \quad \text{.........(2)}$$

where: P_{CO2} and P_{CO} are the partial pressures, and k_1, k_2, k_3 are the experimentally determined rate constants. Although the quantitative validity of this equation has been subject to criticism, it is taken as a basis for consideration of the mechanism of the reaction of carbon dioxide with carbon.

The rate of this reaction is retarded not only by carbon monoxide, but also by the presence of hydrogen in the reaction mixture. When from the possible hypothetical schemes, which satisfy Equation 2, those are eliminated which include stages that have been experimentally shown to be improbable, two basic variants of the reaction mechanism remain:

Variant A

$$C + CO_2 \rightarrow C(O) + CO$$
$$C(O) \rightarrow CO$$
$$CO + C \rightarrow C(CO)$$

Variant B

$$C + CO_2 \rightarrow C(O) + CO$$
$$C(O) \rightarrow CO$$

The basic difference between the two schemes lies in the explanation of the inhibiting effect of carbon monoxide. The rate of the reaction depends on the number of free active sites. In variant A, the rate of the reverse reaction is considered to be negligible and the inhibiting effect of carbon monoxide is supposed to be due to the blocking of active sites by their being covered by the adsorbed carbon monoxide. According to variant B the rate of the reverse reaction is considered to be significant, and the effect of carbon monoxide is explained as being due to a displacement of the reaction equilibrium in the latter equation.

Activation with carbon dioxide involves a less energetic reaction than that with steam and requires a higher temperature 850-1000^{O}C. The activation agent used in technical practice is flue gas to which a certain amount of steam is usually added, so that actually this is a case of combined activation. The catalysts for the reaction with carbon dioxide are carbonates of alkali metals.

- **Activation with Oxygen (air)**

In the reaction of oxygen with carbon both carbon monoxide and carbon dioxide are formed according to the equations:

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -387 \text{ kJ/mol}$$

$$2C + O_2 \rightarrow 2CO \qquad \Delta H = -226 \text{ kJ/mol}$$

Both reactions are exothermic. The mechanism of the reaction of carbon with oxygen is not yet fully understood; the most discussed point is whether carbon dioxide is a primary product of carbon oxidation or the monoxide is formed first and the dioxide is the product of secondary reaction. According to the present state of knowledge it may be assumed that both oxides are primary products. The value of the ratio CO/CO_2 increases with the increase of temperature.

The reactions with oxygen being exothermic, it is not easy to maintain the correct temperature conditions in the oven; it is especially difficult to avoid local overheating which prevents the product from being uniformly activated. Furthermore, because of the very aggressive action of oxygen, burn-out is not limited to the pores but also occurs on the surface of the grains, causing great loss. Carbons activated with oxygen have a large amount of surface oxides.

3.1.2 Porosity

During the process of activation the spaces between the elementary crystallites become cleared of various carbonaceous compounds and disorganized carbon, and carbon is also removed partially from the layers of the elementary crystallites. The resulting voids are called pores. A suitable activation process causes a large number of pores to be formed so that the total surface area of their walls, i.e. the internal surface of the activated carbon is very large, and this is the main reason for its large adsorptive capacity. Activated carbon usually has several groups of pores, each groups having a certain range of values of the effective diameter. Formerly pores can be classified into three groups: micropores, mesopores, and macropores.

Micropores have small sizes comparable with those of adsorbed molecules. Their effective diameter are usually smaller than 2 nm, and average pore volumes of activated carbons usually fall in the range of 0.15-0.5 cm^3/g. In general, the surface area of microporous activated carbons lies between 100-1,000 m^2/g. The energy of adsorption in micropores is substantially greater than that for adsorption in mesopores or at the non-porous surface. In micropores, adsorption proceeds via the mechanism of volume filling.

Mesopores, also known as transitional pores, have effective diameter falling in the range of 2-50 nm. The process of filling their volume with adsorbate takes place via the mechanism of capillary condensation. For average activated carbons, the volumes of mesopores lie between the limits 0.02-0.1 cm^3/g. The peak of the distribution curve of their pore volume versus their radius is mostly in the range of 4-20 nm. For adsorption in liquid phase, activated carbon should have pores size larger than 3 nm in diameter, which falls in the range of mesopores. Besides their significant contribution to adsorption, mesopores also perform as the main transport arteries for the adsorbate.

Macropores are those having effective diameter >50 nm and their volumes are not entirely filled with adsorbate via the mechanism of capillary condensation. The values of their specific surface area are negligibly small when compared with the surface of the remaining types of pore. Consequently macropores are not important in the process of adsorption as they merely act as transport arteries rendering the internal parts of the carbon grains accessible to the molecules of the adsorbate.

3.1.3 Determination of the properties of activated carbon

The properties of activated carbon that usually should be determined are following:

Surface Area:

BET surface area is the surface area that is measured using liquid nitrogen and calculated by BET theory. Surface area is measured from the activated carbon's adsorption and desorption of nitrogen at 77 K. Several assumptions are used in BET theory, such as that the heat of adsorption is constant over the entire surface coverage of the monolayer and that the monolayer is achieved despite the fact that exactly one monomolecular layer is never actually formed.

Porosity:

Pore size distribution can be determined by applying the Dollimore-Heal method to the measured desorption isotherms, and the microporosity is evaluated by t-plot method. Then the mesopore and micropore volumes are determined to evaluate the potential adsorption capacities of the obtained activated carbon.

Adsorption Test:

The adsorption properties of activated carbon are generally estimated by determining the isotherms of adsorption in liquid phase. The test substances that usually used as adsorbates are iodine and methylene blue. Iodine adsorption is an indicator of the capability to remove the taste and odor from water. On the other hand, methylene blue adsorption test evaluates the adsorption capacity for the color in water.

Physico-chemical properties, which generally are determined, are:

Volatile matter, which is the percentage of gaseous products, exclusive of moisture vapor. Volatile matter is determined by establishing the loss in mass resulting from heating an activated carbon sample under rigidly controlled conditions.

Ash content, which consists mainly of oxides, sulfates and carbonates of iron aluminum, calcium and sodium. In specific end uses the amount and composition of ash content may influence the capability and certain desired properties of activated carbon.

Moisture content, which is the water content in activated carbon and it is often required to define and express the water content in relation to the net weight of activated carbon.

Bulk density, which is defined as the mass per unit volume of the activated carbon including both the pore system and the external void space between the particles.

3.2 Adsorption Theory

When two phases are in contact, there is a region at their interface the composition of which is different from that of the bulk of either phase. The increase in the concentration of a substance at the interface as compared with the bulk concentration, is known as adsorption. On the surface of a solid, substances can be adsorbed from a gaseous or liquid phase. The solid is known as the adsorbent and the gas or liquid is called the adsorbate.

Adsorption is brought about by the intereactions between the solid and the molecules in the fluid phase. Two kinds of forces are involved, which give rise to either physical adsorption or chemisorption. Physical adsorption forces are the same as those responsible for the condensation of vapors and the deviations from ideal gas behaviour, whereas chemisorption interactions are essentially those responsible for the formation of chemical compounds. The most important distinguishing features may be summarized as follows:

1. Physical adsorption is a general phenomenon with a relatively low degree of specificity, whereas chemisorption is dependent on the reactivity of the adsorbent and adsorbate.
2. Chemisorbed molecules are linked to reactive parts of the surface and the adsorption is necessarily confined to a monolayer. At high relative pressures, physical adsorption generally occurs as a multilayer.
3. A physisorbed molecule keeps its indentity and on desorption returns to the fluid phase in its original form. If a chemisorbed molecule undergoes reaction or dissociation, it loses its identity and cannot be recovered by desorption.

4. The energy of chemisorption is the same order of magnitude as the energy change in a comoparable chemical reaction. Physical adsorption is always exothermic, but the energy involved is generally not much larger than the energy of condensation of the adsorbate. However, it is appreciably enhanced when physical adsorption takes place in very narrow pores.
5. An activation energy is often involved in chemisorption and at low temperature the system may not have sufficient thermal energy to attain equilibrium fairly rapidly, but equilibration may be slow if the transport process is rate-determining.

The variation of extents of adsorption with relative pressure of the adsorate at constant temperature, is the adsorption isotherm. Next, the variation of extents of adsorption with temperature of adsorption, at constant relative pressure, is the adsorption isobar. Finally, the variation of relative pressure of the adsorbate. with adsorption temperature, to maintain a constant amount adsorbed on the adsorbent is the adsorption isostere.

3.2.1 Adsorption isotherm

The adsorption isotherm provides essential information about the porosity in solids and there are significant variations in isotherm shape. According to IUPAC classification, the shapes of adsorption isotherm are shown in Figure 3.2.1. Type I isotherm is concave to the relative pressure (p/p^o) axis. It rises sharply at low relative pressures and reaches a plateau: the amount adsorbed by the unit mass of solid approaches a limiting value as $p/p^o \rightarrow 1$. The narrow range of relative pressure necessary to attain the plateau is an indication of a limited range of pore size and the appearance of a nearly horizontal plateau indicates a very small external surface area. The limiting adsorption is dependent on the available micropore volume.

Type II isotherm is concave to the p/p^o axis, then almost linear and finally convex to the p/p^o axis. It indicates the formation of an adsorbed layer whose thickness increases progressively with increasing relative pressure until $p/p^o \rightarrow 1$. If the knee of the isotherm is sharp, the uptake at Point B is usually considered to represent the completion of the monomolecular layer and the beginning of the formation of the multimolecular layer.

In Type III, the isotherm is convex to the p/p^o axis over the complete range and therefore has no Point B. This feature is indicative of weak adsorbent-adsorbate interactions.

Type IV isotherm, whose initial region is closely related to the Type II isotherm, tends to level off at high relative pressures. It exhibits a hysteresis loop, the lower branch of which represents measurements obtained by progressive addition of gas of adsorbent, and the upper branch by progressive withdrawal. The hysteresis loop is usually associated with the filling and emptying of the mesopores by capillary condensation.

Type V isotherm is initially convex to the p/p^o axis and also levels off at high relative pressures. As in the case of the Type III isotherm, this is indicative of weak adsorbent-adsorbate interactions. A Type V isotherm exhibits a hysteresis loop which is associated with the mechanism of pore filling and emptying.

Eventually, Type VI isotherm, or stepped isotherm, is associated with layer-by-layer adsorption on a highly uniform surface such as graphite. The sharpness of the steps is dependent on the system and the temperature.

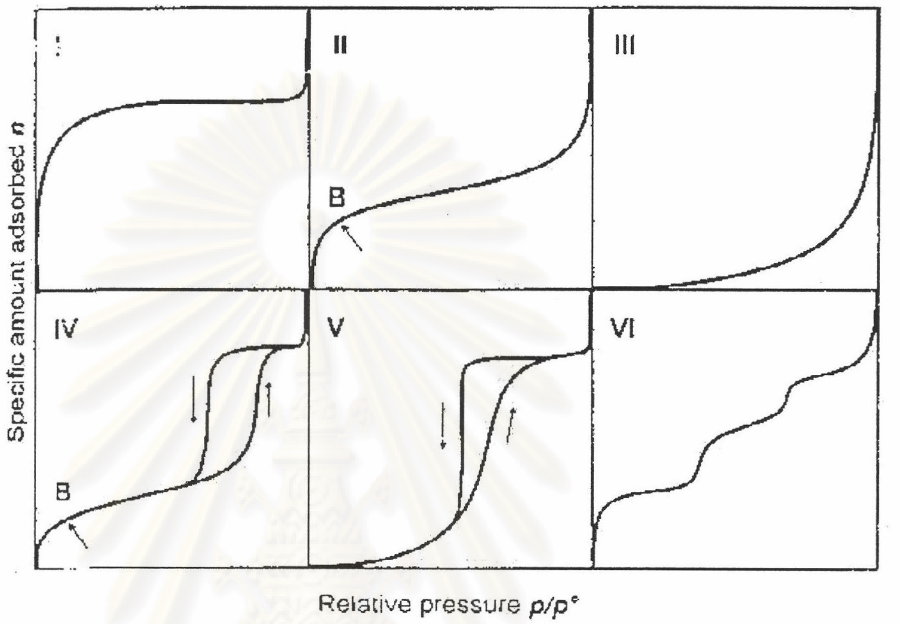

Figure 3.2.1 Shapes of adsorption isotherm

3.2.2 Regeneration

Process employed to restore the adsorptive capacity of spent carbon are known as regeneration. Regeneration of carbon has been conducted in varied ways. Carbons used for vapor phase adsorption are regenerated by passing low pressure steam through the carbon bed to evaporate the adsorbed solvent and convey it to the exit where the steam is condensed and the solvent is recovered in a liquid state. In most cases the adsorptive capacity of the carbon is restored. The principle has been embodied in efforts to regenerate carbon used to remove volatile substances from liquid systems, e.g., the recovery of phenol from coke oven waste liquors. Desorption, the extraction of the adsorbate with a solvent, can restore much adsorptive capacity in some applications. Unfortunately desorption seldom restores the full capacity.

Generally a variety of ingredients are adsorbed from an industrial solution, and because an effort is usually made to obtain selective extraction of the desired substance, it follows the other substances remain as residuals on the carbon. However, it is to be mentioned that instances are known in which better recoveries are obtained by adsorption-desorption when a carbon is reused. A possible explanation is that the initial adsorption saturates areas of the surface on which irreversible adsorptioin occurs, and therefore the reuse involves only those areas from which complete reversible adsorption occurs. In general, regeneration from liquid phase applications is accomplished by thermal means. Spent carbon is directly subjected to oxidation, either with air at 300-600°C or with steam and/or CO_2 at 800-900°C. The carbon recovery was satisfactory and the adsorptive capacity was restored, 90-95% recovery.