

The Surface Chemistry of Active Carbon

A Discussion of Structure and Surface Functional Groups

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■ Active carbon is an effective adsorbent for removal of dissolved organic substances from waters and wastewaters. The physicochemical nature of the surface of carbon is an important factor in the adsorption process, and should be considered in selection or preparation of carbons for specific applications. The principal objective of the present discussion is the review of current information on this subject and development of an elementary conceptual model for description of the active carbon surface. The purpose of this model is to delineate some of the more significant factors to be considered in interpretation of sorption phenomena associated with active carbon, and to provide a basis for further research in this area. Considerations of importance in this model are parameters which influence both the structure and the surface chemistry of the active carbon. There is strong indication of the need for continuing research on the definition of the nature of surface functional groups, and on the particular conditions of preparation which will produce an active carbon best suited for a specific application.

Exacting demands are being made upon existing water resources to meet the requirements of a highly industrialized society. These demands can be expected to mount in the future, for continuing population expansion and technological development lead naturally to both more extensive and more intensive use of available supplies of water, and ultimately to the pollution and degradation of the quality of these waters. Much of the water currently available to a large segment of society has been subjected to previous use. Indeed, multiple reuse of water is not uncommon today; planned and deliberate reuse is expected to be an even more significant factor in water resources management in the years ahead. Evidently, as reuse practice increases, more stringent requirements will be placed on the treatment of waters and wastewaters, and more effective removal of persistent materials, which might otherwise build up to intolerable concentrations during several reuse cycles, will be required.

Adsorption on active carbon has emerged as a particularly attractive method for removal of perdurable organic pollutants from waters and wastewaters. Although active carbon has been widely employed for the past three or four decades for removal of taste- and odor-producing materials from water supplies, its use in this application has been largely occasional

and for the most part quite inefficient. While it has been possible to tolerate such inefficiencies in an application involving relatively low concentrations of pollutants, extensive treatment of wastewater for direct reuse will require that this process be developed to a high degree of effectiveness and efficiency for obvious technological and economic reasons.

In order that engineers responsible for the design of active carbon facilities for water or waste treatment be in position to articulate specifications for maximum efficiency of use in particular situations, they must have at their disposal precise information about the nature and behavior of active carbon and about the adsorption process. Much recent research has centered on the development of such information for this purpose (Johnson *et al.*, 1964; Joyce and Sukenik, 1964; Weber, 1966; Weber and Morris, 1963 and 1964), but there is yet more to be learned and set forth regarding the properties and surface chemistry of active carbon and about factors which affect its behavior as an adsorbent. Active carbon is effective for removal of organic substances of relatively low solubility in water primarily because it provides a large interfacial area at which such substances may accumulate. However, any interpretation of the adsorptive behavior of active carbon based solely on the extensiveness of the surface of this material is obviously incomplete, for equal weights of two carbons prepared from different raw materials and/or by different methods may possess the same total surface area yet function differently as adsorbents. Part of such differences in adsorptive behavior can be explained in terms of relative pore size distributions, but part must also be attributed to differences between the respective surface properties of the carbons. The surface of any active carbon is comprised in part of residual electron- and ion-exchange functional groups, connected by electron-conducting bond systems (Garten and Weiss, 1957b). The nature of these functional groups is determined to a large extent by the method of activation as well as by the type of raw material from which the carbon is prepared. With the existence of electron- and ion-exchange groups at the surface of carbon, it is reasonable to expect that electrolytes in solution may interact with the carbon to influence its behavior as an adsorbent. Indeed, such interactions could markedly affect the over-all adsorption process under certain conditions, possibly effecting changes in the process which may be put to good advantage to achieve higher efficiency or enhanced effectiveness of removal of pollutants. Weber and Morris (1964), for example, have shown that the hydrogen ion activity of a solution affects both rate and capacity for adsorp-

tion of negatively charged species of sulfonated alkylbenzene from aqueous solution by carbon. These authors have interpreted their results as indicating that decreasing pH leads to an increasing association of the positively charged hydrated proton with negatively charged functional groups on the active carbon surface, thus neutralizing electrostatic repulsive forces to allow the charged organic species more easily to migrate through the pore spaces and be adsorbed at inner surface sites. Garten and Weiss (1957b) have interpreted changes in hydrogen ion activity observed upon addition of active carbon to acidic or basic solutions in terms of an interaction between the acid or base and a basic or acidic heterocyclic surface structure, respectively. This interaction is currently being studied in detail in the authors' laboratories to determine more precisely its effect on the sorptive properties of active carbon.

Other inorganic species also seem to be important in their effects on the manner in which active carbon functions in aqueous solution as a sorbent for organic substances. Joyce and Sukenik (1964) have observed a 50% increase in ash content (from 6 to 9% and from 12 to 18%) to be accompanied by a 50% decrease in the capacity of an active carbon after 10 cycles of sorption from a solution of the calcium salt of a sulfonated alkylbenzene followed by thermal regeneration. Because the ash was soluble in acid solution, but insoluble in near neutral solution, these authors suggest that acid treatment in conjunction with thermal regeneration may prove feasible as a means for restoring active carbon to near original capacity. Before such treatment is effected however, one should know how the acid may affect the active carbon surface, and, therefore, how it may influence the adsorption process.

Various chemical oxidizing agents can also interact with active carbon in aqueous solution to increase the amount of chemisorbed oxygen at the carbon surface (Puri *et al.*, 1961). Once more, however, the effect of the presence of this oxygen on the sorptive properties of active carbon has not yet been sufficiently defined.

Apparently, then, much more information is needed regarding the nature of interactions which occur between the various functional surface groups of active carbon and electrolytes in aqueous solution, with particular reference to the effects of such interactions on the sorptive properties of the carbon. The present discussion has as its objective the examination of such information as is currently available concerning the structure and nature of active carbon, and the presentation of a relatively unified concept or model for description of the surface chemistry of this material. This model, hopefully, will provide a reasonable basis for further research directed to the delineation of the surface properties of carbon significant in its applications for water and wastewater treatment.

Preparation of Active Carbon

The term active carbon actually implies a rather broad family of substances, with individual species being characterized by sorptive and catalytic properties rather than by definite structure or specific chemical composition (Hassler, 1963). Particular properties may be imparted to an active carbon either by starting with different raw materials or by utilizing different preparative procedures.

Substances from which active carbons are manufactured are carbonaceous in nature, usually carbohydrates; wood, coal, sugar, nut shells, and vegetable matter are examples of typical raw materials. Differences in active carbons may obtain as a result of the particular characteristics of the starting material, but many of the differences commonly ascribed to dissimilar starting materials may be due in fact to noncarbonaceous impurities. In addition, preparative conditions may be varied and selected additives employed to produce a particular active carbon of desired structure and surface properties.

The production of active carbon involves first the formation of a char from the raw material. The starting material is heated—usually in the absence of air—to a temperature sufficient to effect drying and to drive off volatile fractions. Carbonization is then accomplished by elevating the temperature, producing a carbonaceous char (Johnson *et al.*, 1964; Hassler, 1963). In this process the temperature is increased slowly to allow time for each step to be completed before the next begins. The entire process is usually carried out below 600° C., although exceptions do exist. Additives such as calcium chloride, magnesium chloride, zinc chloride, or any one of a number of similar materials may be used to catalyze the process and to impart certain characteristic properties to the finished product (Hassler, 1963).

The char developed in the carbonization process has relatively little internal surface area, and because a large surface is required for most adsorption applications, the char is generally "activated" by treatment with oxidizing gases under carefully controlled conditions. The oxidizing gases—commonly carbon dioxide, steam, and air—attack the more readily oxidizable portions of the char, resulting in the development of a porous structure and an extensive internal surface. The temperature of activation is a critical factor in the process, as will be discussed in more detail shortly. Treatment of the char with reagents such as chlorine, dolomite sulfates, and several other substances to develop special properties in the finished product and to catalyze the action of the oxidizing gas is often effected prior to the activation process (Hassler, 1963). According to Johnson *et al.* (1964), carbonization and activation can sometimes be carried out in one step, rather than as separate operations. The total surface area of a carbon, by far the greatest percentage of which is internal, can be as great as 2,500 square meters per gram after activation.

Structure and Structural Development

The molecular and crystalline structure of active carbon is an important determinant of the types of functional groups which can exist on the surface and is, therefore, an important consideration in any discussion of the surface chemistry of this material. Although there is little direct information available on the structure of active carbon, much can be derived from existing data on the structure of carbon black. Very little chemical difference exists between these two substances, and the only apparent physical difference is that the carbon black has much less internal surface area (Garten and Weiss, 1957b).

As a basis for discussion of the active carbon structure, it is appropriate to consider first the structure of ideal graphite in that it is closely approximated in the basic structural unit of both active carbon and carbon black (Wolff, 1959; Heckman, 1964; Walker, 1962).

The structure of ideal graphite is given in Figure 1. According to Walker (1962), this structure is composed of a system of infinite layers of fused hexagons. Within each layer the carbon-carbon bond distance is 1.415 Å, indicating one-third double bond character. Three of the carbon's four electrons are engaged in forming regular covalent bonds with neighboring atoms and are localized, while the fourth resonates between several valence-bond structures, giving each carbon-carbon bond a one-third double bond character. Relatively weak van der Waals forces act between the parallel layers to hold the distance of separation to approximately 3.35 Å. The carbon layers form an *a-b-a-b-a-b* stacking sequence in which one-half of the carbon atoms in any one plane lie above the center of the hexagons in the layer immediately below it. The carbon atoms are directly superimposed in alternate layers. X-ray diffraction spectra obtained for most natural graphites indicate that this structural configuration is in fact predominant (Walker, 1962).

During the carbonization of the raw material in the preparation of active carbon, small aromatic nuclei, interpreted from x-ray spectrographs as microcrystallites consisting of fused hexagonal rings of carbon atoms having a structure similar to that of graphite, are formed (Wolff, 1959; Heckman, 1964). The diameter of the planes making up the microcrystallite has been estimated as 20 to 50 Å. (Wolff, 1959). The height of stacking is also in the range of 20 to 50 Å., indicating that each microcrystallite consists of 5 to 15 layers of aromatic planes.

Although the structure of the microcrystallite is similar to that of graphite, it differs in many ways. During the formation of the microcrystallite, impurities should be expelled from its interior. However, Walker (1962) states that interior vacancies exist in the microcrystallite and that their formation depends on the method of preparation. Possibly these vacancies contain some of the impurities; the presence of impurities may, in fact, influence the formation of such a vacancy. In addition, the ringed structures at the edges of the planes making up the microcrystallite are often heterocyclic owing to the nature of either the starting material or of the preparation process used (Garten and Weiss, 1957b). Heterocyclic groups would tend to affect both the distance of separation of adjacent planes and the sorptive properties of the carbon. Also, orientation between adjacent planes in the microcrystallite varies from that found in ideal graphitic structure to that of complete random orientation found in turbostratic carbons (Walker, 1962). The definite *a-b-a-b-a-b* stacking order, therefore, does not exist in most active carbons. Functional groups terminating the microcrystallite planes interconnect the microcrystallites, and are at least partially responsible for the turbostratic character in that they prevent orientation of the planes with respect to each other. Because of its special properties and the many differences between it and graphite, Garten and Weiss (1957b) have chosen to compare active carbon with a complex organic polymer rather than with a graphitic type particle.

The structure of the char particle is developed further by

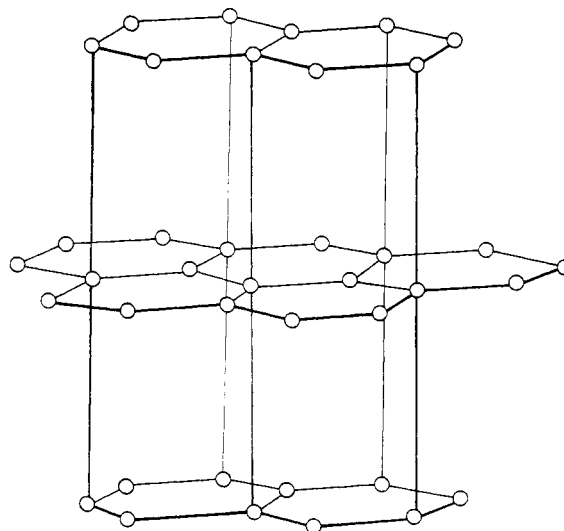


Figure 1. The arrangement of carbon atoms in the graphite crystal (Walker, 1962)

treatment with oxidizing gases at high temperature during the activation process. Dubinin *et al.* (1964), noticed two stages of oxidation in the activation of carbonized sucrose. First, macropores were formed by the burnout of the most reactive material, consisting principally of hydrocarbon radicals attached to the edge carbons of the microcrystallite. Second, micropores were formed mainly by the burnout of microcrystallite planes. The diameter of the micropore is generally on the order of 4 to 10 Å., while the macropore diameter is usually much larger (Wolff, 1958). The majority of internal surface area is contributed by the walls of the micropore. Snow *et al.* (1959), reported that higher ash content causes faster pore development during activation. Inorganic matter appears to cause stress localizations on the surface of the microcrystallite at which points oxidation is initiated much more easily. Once a plane is attacked by an oxidizing gas, oxidation of that plane continues in preference to another area until a stable structure is developed (Wolff, 1959).

Carbonization and activation temperatures are significant considerations in the structural development of active carbons. Riley (Garten and Weiss, 1955) has demonstrated that the size of the microcrystallites of carbons prepared from carbohydrates increases with increasing temperature of carbonization. In addition, the mechanical strength and electrical conductivity of a carbon increase when prepared at temperatures above 700° C. The temperature at which activation is effected is important also because carbonization continues during this process via the mechanisms of actual removal, cracking, or cyclization of functional groups present at the edges of the microcrystallite (Wolff, 1959).

Chemical Nature of the Active Carbon Surface

If we proceed on the basis of the structure outlined above, and neglect for the moment the effects of noncarbonaceous impurities, two major types of surfaces can be postulated for active carbon: the planar surfaces of the microcrystallites and the edges of the carbon planes making up the sides of the microcrystallite.

The planar surfaces are probably relatively uniform in

nature. No attached functional groups should be present because the electrons of the carbon atoms are involved in covalent bonding with neighboring carbon atoms. Because oxidation occurs much more readily at the edge of the carbon plane than on the surface of the plane (Hennig, 1962), few vacancies owing to oxidation during the activation process are expected in the surface plane. The majority of the sorptive processes occurring on this surface would be due then to the relatively weak van der Waals forces, although electrons are available for π -bonding if the sorbate is capable of entering into such a bond (Gasser and Kipling, 1960). Because most of the surface area of a carbon particle is found in the micropores, and because micropores are formed by the "eating out" of microcrystallite planes (Wolff, 1959), the larger percentage of the total surface area is probably of the planar surface type.

The sides of the microcrystallites are more heterogeneous than the planar surfaces, and are characterized by various types of functional groups and vacancies owing to the action of oxidizing gases. Corners or raised positions on the surface have the greatest tendency to participate in the electron-sharing reactions which characterize chemisorption (Zettlemoyer, 1959). Sorption in depressions is probably physical in nature, but the bonds formed in this case should be much stronger than the bonds formed in physical sorption on the planar surface of the microcrystallite.

Although surfaces of the preceding types can be expected for a very pure active carbon, many carbons have large percentages of oxygen, hydrogen, and inorganic ash. The concept of the type of surface available for sorption must be modified somewhat when such substances are present. The presence of hydrogen on the surface of active carbon, for example, lends quite definite properties to that surface. Certain sorption reactions are known to be more or less specific for surfaces comprised of hydrogen sites. Kipling and Shooter (1966) reported that iodine vapor adsorption on Spheron 6 can be interpreted in terms of adsorption, on that part of the surface covered with hydrogen sites, to the exclusion of those portions of the surface covered with oxygen-containing functional groups. Hydrogen presumably exists either in the form of terminal groups on the fused aromatic planes of the microcrystallite or as part of the hydrocarbon functional groups attached to these planes (Wolff, 1959). Wolff (1958) reported that hydrogen is present in amounts ranging from eight to 19 times that of oxygen, on a molar basis, for carbons containing 0.94 to 2.25% oxygen by weight.

Inorganic matter is present in most commercial active carbons to a very significant extent, and its presence has many noticeable effects (Hassler, 1963; Wolff, 1958). The total amount present consists of inorganic constituents originally present in the starting material and various inorganic salts added to catalyze the carbonization and activation processes or to impart special sorptive properties such as selectivity to the active carbon. The fact that strong acid will remove almost all of the ash content of active carbon suggests that the inorganic matter exists primarily on the microcrystallite

surfaces (Wolff, 1958; Blackburn and Kipling, 1955). The special properties which the inorganic salts develop possibly are due to their effect on the active carbon surface and to their interactions with the sorbate or other solution constituents. Sorption on a surface covered with tightly held inorganic species would very likely differ in nature from sorption on an active carbon surface free of such species. Pore structure would also be affected differently by different types of salts used to catalyze the activation process. Possible interactions between the inorganic salts on the active carbon surface and the sorbate or other solution constituents include complex formation, ion-pair formation, precipitation reactions, and oxidation-reduction reactions. Basic studies of the sorptive properties of active carbon should include a careful study of the effect of the active carbon's inorganic constituents.

Electron spin resonance studies of active carbon have suggested free radical structures or structures with unpaired electrons in the microcrystallite (Harker *et al.*, 1961). According to Ingram (1959), large numbers of unpaired electrons are trapped during the carbonization period owing to bond breakage at the edges of the planar structures. These electrons are resonance stabilized. Studies by Harker *et al.* (1961) indicated that oxygen interacts with these electrons to form oxygen complexes on the surface. The only means by which this oxygen can be removed is as oxides of carbon by degassing at high temperature.

Oxygen, one of the major noncarbon constituents of active carbon, constitutes 2 to 25% by weight of this material, the exact amount present depending upon the temperature and method of activation (Wolff, 1959). The temperature of activation ranges from 400° to 1200° C., and the oxygen content decreases with increasing temperature of activation (Garten and Weiss, 1957a). Heating carbon at a temperature of 1000° to 1200° C. in a high vacuum removes nearly all of the oxygen from the carbon surface, usually as oxides of carbon. For this reason oxygen is thought to exist in structures on the surface of the microcrystallite or between carbon planes near the surface of the microcrystallite (Garten and Weiss, 1955).

The presence of oxygen complexes on the surface of the carbon affects the sorptive properties of this material in that they tend to increase the polarity of the surface (Barrer, 1966). In aqueous solution, therefore, a stronger solvent-active carbon bond must be broken before sorption of the sorbate can occur if oxygen complexes exist at the carbon surface. Excluding any specific oxygen complex-sorbate interaction, increased polarity decreases the quantity of nonpolar sorbate removed from solution by the carbon. For a polar sorbate, the oxygen complex-sorbate interaction usually is stronger, compensating, at least in part, for the added energy required to desorb water. Kipling (1957) discovered that oxygen on the surface of carbon affects the specificity of sorption from an organic, binary liquid solution. As indicated previously, Kipling and Shooter (1966) reported that iodine apparently does not adsorb on that portion of the active carbon surface

covered with oxygen sites, but does adsorb on the part of the surface covered with hydrogen sites. These authors also indicate that the normally strong lateral interactions of adsorbed iodine molecules appear to be lessened in the presence of the oxygen, thus preventing attainment of the extent of uptake realized in the absence of surface oxygen. An additional consideration is that sorbates which have a natural tendency to combine with oxygen probably sorb more easily on oxygenated surfaces than they do on nonoxygenated surfaces.

Oxygen can be added to an active carbon in one or more of three principal ways. If the starting material contains oxygen, this may become incorporated into the microcrystallite surface structure during the manufacture of the carbon (Garten and Weiss, 1955). If the starting material is a carbohydrate, for example, heating will cause condensation and cyclization of the carbohydrate with the inclusion of an oxygen atom in the ringed structure as an ether oxygen. As a second possibility, oxygen can be sorbed on active carbon at room temperature. Part of the oxygen added in this manner can be evacuated at room temperature—this phenomenon being known as “the reversible effect”—while another part requires evacuation at temperatures in excess of 1000° C. (Harker *et al.*, 1961). The latter phenomenon, which has been studied by electron spin resonance methods, is known as “the surface oxide effect.” Thirdly, oxygen can be chemisorbed on the surface of the active carbon during treatment with oxidizing agents. As previously indicated, the principal oxidizing gases in the activation process are air, steam, and carbon dioxide. These three gases form oxygen complexes at the surface of the carbon which can be removed—as carbon monoxide, carbon dioxide, and water vapor—only by degassing at very high temperatures (Hassler, 1963; Puri *et al.*, 1958). Treatment of active carbon with chemical oxidizing agents in aqueous solution also leads to the chemisorption of oxygen on the surface of the carbon (Puri *et al.*, 1958, 1960, and 1961).

Characterization of Oxygen Surface Structures

Because of their numbers and their probable effects on the sorption process, oxygen complexes on the surface of carbon merit careful consideration. An excellent review of this topic has been given by Boehm (1966); anyone contemplating further work in this area should consult this review.

One of the principal methods for study of the nature of oxygen structures on carbon has been by simple acidimetric-alkalimetric titrations, and major interest has focused on the very important variable of temperature of activation (Boehm, 1966; Garten and Weiss, 1957b). Garten and Weiss (1957b) have provided an excellent review on the findings of such research, and these may be summarized briefly as follows:

Carbon activated at 400° C. (L-carbon) will sorb base but not acid from aqueous solution while carbon activated at 800° to 1000° C. (H-carbon) will sorb acid but not base.

Carbon activated at intermediate temperatures will sorb both acid and base.

Capacities for both acid and base are usually in the milli-equivalent per gram range, but this value depends on the substances added to the carbon during the activation process.

Similar to ion exchange resins with basic and acidic functional groups, respectively, H-carbons produce a basic pH in solution, while L-carbons yield an acidic solution pH

(Garten and Weiss, 1957b). Since no acid or base can be extracted from the solution after contact with the carbon, the conclusion is made that surface structures are responsible for this phenomenon. Electrokinetic studies have indicated that H-carbons exhibit a positive surface potential, as opposed to a negative surface potential for L-carbons. However, unless care is taken to cool H-carbons in an inert atmosphere after activation, formation of structures which change the potential from positive to negative does occur. The presence of inorganic constituents at the surface may also affect the potential to the point of reversing its sign from that which might be expected on the basis of the activation temperature.

A negative potential for L-carbons is consistent with the presence of surface acids, while the existence of a positive potential for H-carbons requires further consideration. Garten and Weiss (1957a and 1957b), using various techniques for the study of L-carbons, have concluded that surface acids responsible for the sorption of alkali from aqueous solution consist of at least three fundamental types: phenol; *n*-lactone; and *f*-lactone—the type present in fluorescein and phthalein dyestuffs (Garten *et al.*, 1957). The relative proportions of these three groups vary with the method of preparation of the active carbon.

In determining the total number of acid groups present on L-carbons by alkalimetric titrations, Garten *et al.* (1957) noted that the titration curves closely resembled the type obtained for weak acids and were comparable with that for titration of a phenolic functional group ion exchange resin. These observations point to the possibility of phenolic surface structures, as illustrated in Figure 2. By way of additional evidence, a certain proportion of the acidic groups have been methylated with diazomethane, but the methoxyl group thus introduced resists hydrolysis when treated with boiling dilute acid. This behavior is characteristic of the phenolic structure (Garten *et al.*, 1957; Boehm, 1966). Conversely, a portion of the total number of acidic groups have resisted methylation with diazomethane, while supplementary infrared spectroscopy studies have produced data consistent with the postulation that these groups are of the *n*-lactone type given in Figure 3, with an absorption band at 1710 cm.⁻¹

A third fraction of the acidic groups on L-carbons was methylated with diazomethane, but with the methoxyl group thus formed being hydrolyzable in dilute boiling acid (Garten *et al.*, 1957). Carbon compounds which have phenolic groups in association with lactone groups, as in fluorescein or phthalein dyestuffs, act similarly. Figure 4 gives illustration of the structure of such lactones, called *f*-lactones, as well as some of the reactions of this group (Garten *et al.*, 1957). The infrared data referred to previously have also revealed an absorption peak at 1750 cm.⁻¹, consistent with the presence of *f*-lactones.

While simple alkalimetric titration has been used rather extensively for measurement of the total number of acid groups present on carbon, some questions have been raised as to the quantitiveness of this procedure. For example, Studebaker (1963), using sodium aminoethoxide in ethylene diamine as a titrant and comparing his results with those obtained by NaOH-titration of active carbon in aqueous solution, has discovered that alkalimetric titration determines only about 68% of the total acidity as measured by the aminoethoxide titration.

Quinone groups are also known to be present on the surface

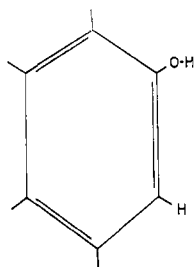


Figure 2. A phenolic surface structure (Garten and Weiss, 1957b)

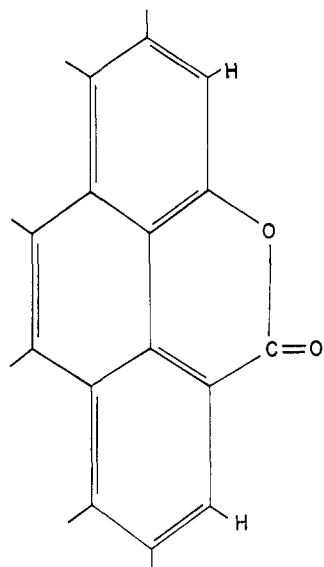


Figure 3. A *n*-lactone surface structure (Garten and Weiss, 1957b)

of active carbon (Garten and Weiss, 1957b and 1961; Studebaker, 1961). An H-carbon cooled in nitrogen gas after activation does not sorb base, but reduction of the H-carbon with sodium borohydride develops base sorbing properties (Garten and Weiss, 1961; Studebaker, 1961). This observation can be explained in terms of quinone reduction to hydroquinone. Hallum and Drushel (1958) also found polarographic evidence for quinones. Reduced quinones, or hydroquinones, might be expected to behave as phenols when treated with diazomethane and thus would be included in the phenolic fraction given by the method of analysis used by Garten and Weiss.

Although a carbon activated at a temperature of 800° to 1000° C. will sorb acid, evacuation at the temperature of activation followed by cooling in an inert atmosphere will so affect the carbon that it will not sorb acid from a deaerated solution until oxygen is admitted (Garten and Weiss, 1957a). Indeed, an exponential relationship exists between the acid sorbed and oxygen partial pressure for the range of 0 to 20 mm. of Hg. Kolthoff (1932) discovered that hydrogen peroxide is released by carbon to a solution from which acid is adsorbed (Garten and Weiss, 1961). Garten and Weiss (1957a), on the basis of this phenomenon, propose the presence of chromene (benzpyran) groups on the H-carbon surface. As illustrated in Figure 5, this structure contains an activated $>\text{CH}_2$ or $>\text{CHR}$ group which can react with a strong acid and oxygen (Wawzonek, 1950). There is much difficulty

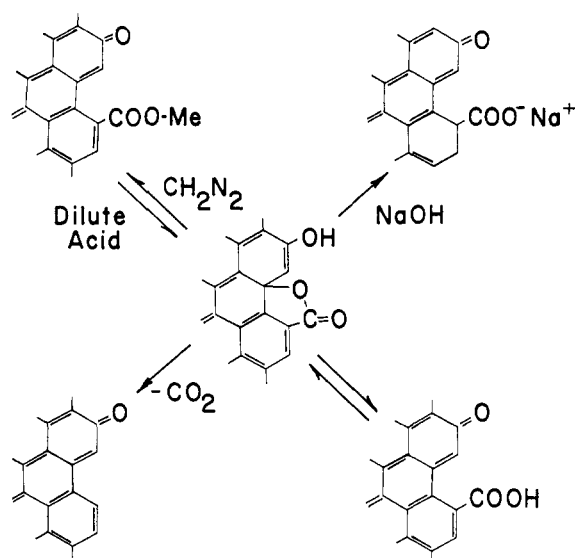


Figure 4. Some reactions of fluorescein-type lactones (Garten *et al.*, 1957)

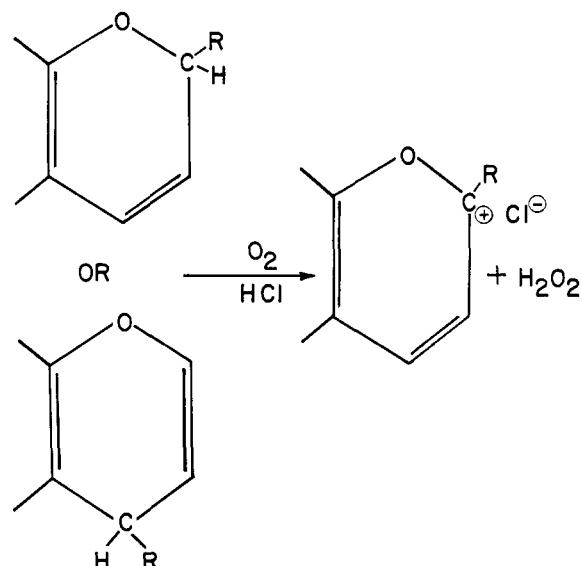


Figure 5. The chromene-acid reaction (Garten and Weiss, 1957a)

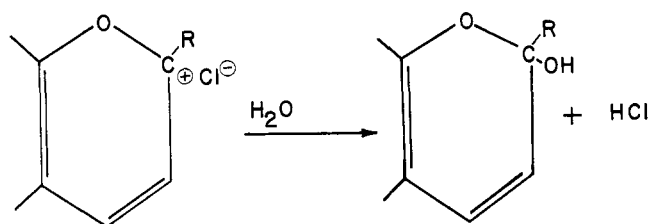


Figure 6. Hydrolysis of the carbonium ion (Garten and Weiss, 1957a)

in establishing the stoichiometry of this reaction, however, because active carbon also catalyzes the breakdown of the hydrogen peroxide (Garten and Weiss, 1957a).

The carbonium ion formed by acid reaction with the chromene group, as shown in Figure 5, will hydrolyze readily in water to form the chromenol group illustrated in Figure 6, a weakly basic group having a dissociation constant of 10^{-11} (Sondheimer, 1953). The fact that the carbonium ion tends to associate so strongly with a negative ion could account for the fact that sorbed acid is very difficult to wash from carbon (Garten and Weiss, 1957a).

In addition to the evidence for chemisorption and the chromene groups, there is also strong evidence that some physical sorption of acid takes place. Garten and Weiss (1957b) have shown that a portion of the sorbed acid on an acid-saturated carbon can be displaced by strongly adsorbed organic molecules. The assumption is made that the physically sorbed acid can be displaced and the chemisorbed acid can not. By this means, an approximation can be made of the number of chromene groups present on the carbon surface. The relative proportion of the quantity of acid physically sorbed to that chemically sorbed again depends on the method of preparation, especially the length of time the carbon is activated.

Discussion

An attempt was made to describe an elementary conceptual model for explanation of some surface properties of active carbon. In the development of this model, it has been necessary to examine the basic structural unit of active carbon, the microcrystallite, and those factors which affect its formation during the manufacturing process. Production variables such as raw material, temperatures of carbonization and activation, additives used for catalysis of carbonization and activation or for the development of specific sorptive properties all seem important in establishing the course of formation of the microcrystallite, and thus the active carbon surface.

Pore surfaces of active carbon appear to consist principally of either the planar or the edge surfaces of the microcrystallite. The planar surfaces are relatively homogeneous, but the edge surfaces are heterogeneous, quite probably covered with oxygen- and hydrogen-containing functional groups. Some of the oxygen complexes appear to be highly reactive with certain inorganic species in aqueous solution, particularly acids and bases. This interaction can be especially significant for active carbons having appreciable quantities of surface oxygen, since it probably results in changes in the nature of the pore surface.

Ash content, which is appreciable for most commercial carbons, might also be expected to affect markedly the nature of the active carbon surface if the inorganic species are distributed over the internal surface of the pores. If the ash is localized in specific vacancies rather than distributed over the pore interior, however, the sorptive properties are likely to be affected very little.

The purpose of this initial model is to set forth some of the more significant interfacial factors and mechanisms to be considered in interpretation of sorption phenomena associated with active carbon in aqueous solutions and to provide a basis for further research aimed at more thorough delineation of sorption processes.

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