ACTIVE CARBON

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MARCEL DEKKER, INC. **New York and Basel**

Library of Congress Cataloging-in-Publication Data

Bansal, Roop Chand
Active carbon.

Includes indexes.
1. Carbon, Activated. I. Donnet, Jean-Baptiste.
II. Stoeckli, Fritz. III. Title.
TP245.C4B35 1988 622'.93 88-3571
ISBN 0-8247-7842-1

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

Current printing (last digit):
10 9 8 7 6 5 4 3 2 1

PRINTED IN THE UNITED STATES OF AMERICA

Preface

Activated carbons are unique and versatile adsorbents because of their extended surface area, microporous structure, universal adsorption effect, high adsorption capacity, and high degree of surface reactivity. They are extensively used to purify, decolorize, deodorize, dechlorinate, and detoxicate potable waters; for solvent recovery and air purification in inhabited spaces such as restaurants, food-processing, and chemical industries; in the purification of many chemical and foodstuff products; and in a variety of gas phase applications. They are also increasingly being used in hydrometallurgy for the recovery of gold and silver and other inorganics and in the treatment of domestic and industrial wastewaters. Their use in medicine for certain types of bacterial ailments is well known. Thus active carbons are of interest in many economic sectors and concern industries as diverse as food processing, pharmaceuticals, chemical, petroleum, mining, nuclear, automobile, and vacuum manufacturing.

Some of these applications are very demanding with regard to the surface chemistry and the surface characteristics of these adsorbent carbons. In the past, many users of active carbon were able to get along with any grade of carbon and were concerned only with the price. The current emphasis, however, is toward unit operations which tend to utilize the entire adsorption space of the carbon, and this puts a high premium on quality, reproducibility, adsorption capacity, and surface reactivity. It was assumed until some years ago that investigation of the fine structure of carbon surfaces was necessary only in particular fields of technological research and in the manufacture of carbons. Today it is realized that characterization of the carbon surface and its porous structure with respect to the chemical composition of the surface, pore size distribution, and surface area is of vital importance whenever quantitative data for processes occurring or starting at the surface of the carbon, such as surface reactions, adsorption, degasing, and surface treatment, are required. A more precise knowledge of the surface chemistry of carbon surface is also essential for the proper development and improvement of active carbon for specific applications. As a maximum in the specific surface area now appears to have been realized, there is need, therefore, to modify carbon surfaces and their porous structure by different surface treatments to develop newer carbons with adequate porosity and with modified properties to cope with new problems and recent developments in the area of wastewater treatment, where large quantities of active carbons are likely to be used. It is with these views that the present book has been conceived.

The book describes briefly the basic steps involved in the manufacture of activated carbons, the selectivity and suitability of different raw materials, and the probable mechanism of the physical and chemical activation processes. The chapter on chemical structure presents an exhaustive survey of the nature and the characteristics of the carbon–oxygen surface structures on acidic and basic carbons and their estimation by physical, chemical, and physicochemical techniques, which include ESCA and the latest innovations in infrared spectroscopy. The chapter on porous structure includes the classification of pores, their characterization and contribution to surface area, distinction between internal and external surfaces, their contribution to the adsorption of gases and vapor, and the thermodynamic consequences of Dubinin's micropore volume theory. The characterization of adsorbent carbons by immersion calorimetry, by adsorption of polar and nonpolar vapors, and by adsorption from solutions is discussed. The importance of active sites and their characterization and of active surface area and its measurement in determining the reactivity of carbons is emphasized. The procedures for the modification of carbon surfaces by surface impregnation, oxidation, halogenation, hydrogenation, and sulfurization are described, and the influence of these surface modifications on the surface characteristics and surface behavior of carbons is discussed.

The book presents a detailed survey of some of the applications utilizing bulk amounts of carbons. The factors involved in the application of activated carbons for the removal of organics and inorganics from the aqueous phase are delineated; the use of activated carbons for the recovery of gold and silver from their cyanide solutions and their elution from the carbon surface are discussed; and the various theories of gold recovery are reviewed. The possibility of using carbons as a catalyst for certain oxidation, combination, decomposition, halogenation, and dehalogenation reactions is also examined. The book thus combines in one volume the manufacture, various facets of the surface chemistry, characterization, and modifications, and the important applications of adsorbent carbons so that carbon scientists and technologists can take full advantage of carbon surfaces and their modifications promoting a relationship between carbon surface structure, carbon surface properties, and their applications and can have access to the relevant literature. The unified approach promotes further research toward improvement and development of newer carbon adsorbents.

We express our thanks to our colleagues Dr. P. Ehrburger, Dr. J. Lahaye, and Dr. Derai for making Professor Bansal comfortable during his stay in Mulhouse; to F. Muller for photography; and to Miss Caty Bachmeyer for typing the manuscript. The authors are also grateful to the Pergamon Press; Academic Press, London; Society of Chemical Industry, London; Butterworths; Ann Arbor Science Publishing; the Council of Mineral Science and Engineering, South Africa; South African Institute of Mining and Metallurgy; and various authors for permission to reproduce figures and tables. Professor Bansal is also thankful to the Centre National de là Recherche Scientifique CNRS (French Ministry for University and Research) for the financial support for his stay and the Panjab University, Chandigarh, India for granting leave. Most important, the understanding, support, and encouragement of our wives, Rajesh Bansal, Suzanne Donnet, and Helen Stoeckli-Evans, made the completion of this project possible.

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Introduction

The term *activated carbon* in its broadest sense includes a wide range of amorphous carbon-based materials prepared to exhibit a high degree of porosity and an extended interparticulate surface area. These are obtained by combustion, partial combustion, and thermal decomposition of various carbonaceous substances. These materials may be granular or in powdered from. The granular form is characterized by a large internal surface and small pores, whereas the finely divided powdered form is associated with larger pore diameters but a smaller internal surface.

The use of activated carbon in the form of carbonized wood dates back many centuries. The Egyptians used it around 1500 B.C. as an adsorbent for medicinal purposes and also as a purifying agent. The ancient Hindus in India filtered their drinking water through charcoal. The basis for the industrial production of active carbons, however, was established in 1900–1901 in order to replace bone char in the sugar refining process. This active carbon was prepared by carbonizing a mixture of materials of vegetable origin in the presence of metal chlorides or by the action of carbon dioxide or steam on charred materials. Activated carbons with better decolorizing power were prepared by the action of zinc chloride on wood and other materials of high carbon content. The manufacture of better quality gas-adsorbent carbons received fresh impetus during World War I, when they were used in gas masks for protection against poisonous gases. In the late 1930s the activated carbons were also manufactured, from sawdust by chemical activation with zinc chloride, for volatile solvent recovery and for the removal of benzene from tower gas.

Activated carbons are excellent adsorbents and thus are used to purify, decolorize, deodorize, dechlorinate, detoxicate, filter, or remove or modify the salts, separate, and concentrate in order to permit recovery; they are also used as catalysts and catalyst supports. These applications of active carbons are of interest to most economic sectors and concern areas as diverse as the food, pharmaceutical, chemical, petroleum, mining, nuclear, automobile, and vacuum industries as well as the treatment of drinking water, industrial and urban wastewater, and air and gas. Nearly 80% (220,000 tons/yr) of the total active carbon is consumed for liquid phase applications where both the granulated and the powdered forms of active carbon are used. The use of powdered carbon is more ancient and generally involves processing of food and drinking water. The total consumption of active carbon in gas phase applications is around 60,000 tons/yr, which includes exclusively the granular form of the active carbon, which may be extruded or pounded, the principal uses being in the purification of air, recovery of gold, and cigarette filters. The consumption of active carbons is high in the United States and Japan, which together consume two to four times more active carbon than the Western European countries. The per capita consumption of active carbon per year is 0.5 kg in Japan, 0.4 kg in the United States, 0.2 kg in Europe, and 0.03 kg in the rest of the world.

The adsorbent properties of activated carbons are essentially attributed to their large surface area, a high degree of surface reactivity, universal adsorption effect, and favorable pore size, which makes the internal surface accessible, enhances the adsorption rate, and enhances mechanical strength. The most widely used commercial active carbons have a specific surface area of the order of 800–1500 m^2/g. This surface area is contained predominantly within micropores, which have effective diameters smaller than 2 nm. In fact, a particle of active carbon is made up of a complex network of pores which have been classified into micropores (diameters < 2 nm), mesopores (diameter between 2 and 50 nm), and macropores (diameters > 50 nm). The macropores do not contribute much toward surface area but act as conduits for the passage of the adsorbate into the interior mesopore and the micropore surface where most of the adsorption takes place. The pore size distribution in a given carbon depends on the type of the raw material and the method of manufacture of the carbon (Fig. 1).

The large surface area of the active carbon is the result of the activation process in which a carbonaceous char with little internal surface is oxidized in an atmosphere of air, carbon dioxide, or steam at a temperature between 800 and 900°C. This causes the oxidation of some of the regions within the char in preference to others so that as combustion proceeds a preferential etching occurs, resulting in the development of a large internal surface area, which in some cases may be as high as 2500 m^2/g.

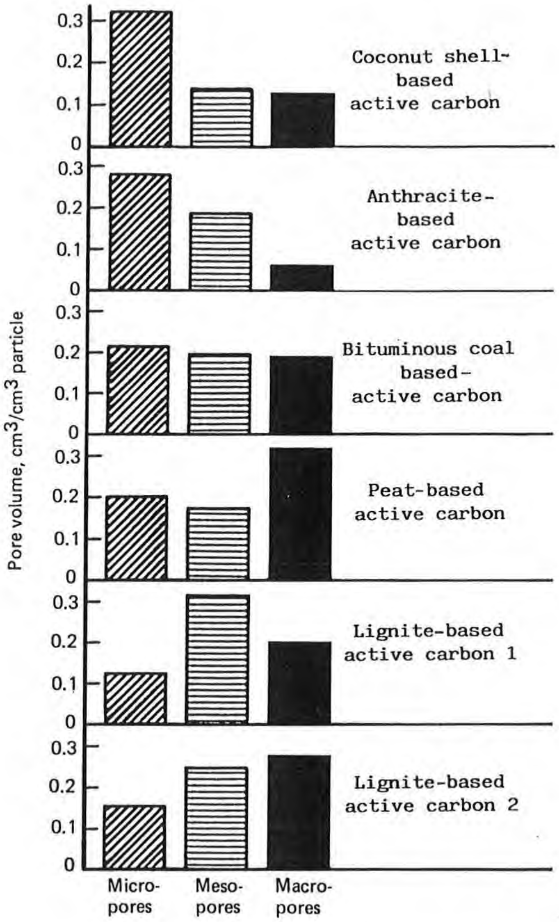

Figure 1 Pore size distribution in some active carbons obtained using different precursors.

The structure of activated carbons has been repeatedly compared with that of graphite and considered to be microcrystalline. However, in recent years transmission electron microscopy of carbonaceous materials has shown that the analogy with graphite is very poor and that the active carbon structure can be visualized as stacks of flat aromatic sheets crosslinked in a random manner (see Fig. 1 of Chapter 3). Activation by carbon dioxide or steam in the range 800–900°C reduces the number of these aromatic sheets in the original stacks, leaving in some cases single and in general nonplanar layers.

Electron spin resonance studies have revealed that the aromatic sheets in active carbons contain free radical structures or structures with unpaired electrons. These unpaired electrons are resonance stabilized and are trapped during the carbonization process as a result of the breaking up of bonds at the edges of the aromatic sheets thus creating edge carbon atoms. These edge carbon atoms have unsatisfied valencies and can thus interact with heteroatoms such as oxygen, hydrogen, nitrogen, and sulfur, giving rise to different types of surface functional groups. Thus the elemental composition of a typical activated carbon was found to be 88% C, 0.5% H, 0.5% N, 1% S, and 6–7% O, the balance representing inorganic ash constituents. The oxygen content of an activated carbon can, however, vary between 1 and 25%, depending on the type of raw material and the conditions of the activation process. The oxygen content of an activated carbon decreases with an increase in temperature of activation, the contents being minimum when the activation temperature is 1000°C or higher. The oxygen is picked up by the carbon from the raw material or from the oxidizing gases (CO_2, O_2, or steam) used for their activation.

The activation temperature significantly influences the nature of the carbon–oxygen surface complex. At low temperature of activation the carbon–oxygen surface complexes formed are less stable and are removed as carbon dioxide on heat treatment in vacuum or in nitrogen. On the other hand, when the temperature of activation is high, the functional groups formed are more stable and could be removed only as carbon monoxide, also at higher temperatures.

Extensive investigations using varied chemical and physicochemical techniques have been reported from several laboratories. The low-temperature–activated carbons have been found to develop acidic surface functional groups which are hydrophilic in character and show negative zeta potential. These acidic surface groups have been identified as phenolic, carboxylic, lactonic, cyclic peroxides, and carbonyl groups. The carboxylic and lactone groups render the carbon surface polar in character and tend to decrease the adsorption of nonpolar aromatic compounds, whereas the carbonyl groups in the form of quinones and hydroquinones tend to enhance the adsorption of aromatic compounds through the formation of an electron acceptor–donor complex. The carbon activated at higher temperature (800–1000°C) develops basic oxides and exhibits positive zeta potential. These basic surface oxides have been suggested to have chromene and pyronelike structures.

Besides oxygen, the activated carbons are invariably associated with hydrogen, which is present partly in the surface oxygen functional group and partly combined with the carbon atoms and dispersed in the granules of the carbon particles. The hydrogen is bonded more strongly than oxygen and cannot be removed completely even on evacuating at 1200°C, when about 30% of the total hydrogen is left behind in the carbon. Infrared studies of some anthracites have shown that the hydrogen is present both in the aliphatic and the aromatic forms. The aromatic hydrogen is bonded covalently to the carbon atoms at the periphery of the aromatic sheets while the aliphatic hydrogen may be present as aliphatic chains and alicyclic groups attached to the peripheral aromatic rings.

The characterization of activated carbons is carried out on the basis of several physical and chemical properties, commonly including their surface area, pore size distribution, impact hardness, ability to adsorb several selected substances such as benzene, carbon tetrachloride, nitrogen from the gaseous phase as well as iodine, molasses, phenol, and methylene blue from the aqueous phase. The nitrogen BET value, for example, expresses the surface that can be covered by nitrogen in a monomolecular layer. Typical nitrogen BET surface area values are found to be between 400 and 1500 m^2/g, the former representing low-activity carbons and the latter, high-activity carbons. However, surface area measurements alone are not sufficient to characterize a carbon product since the nitrogen molecule is very small and can penetrate into pores which are not available for larger molecules. The accessibility of larger molecules that are involved in the actual use of activated carbons may be small compared to adsorption of nitrogen. Furthermore, the adsorption of nitrogen being carried out at very low temperature (-195°C), the nitrogen adsorption cannot measure some of the extremely ultrafine microcapillary pores. Thus the BET surface area should be used with caution. It is essential, therefore, that characterization of carbons be carried out by their adsorption capacity toward larger molecular species such as phenol, iodine, methylene blue, and molasses, under standard experimental conditions. The adsorption capacity of activated carbons toward these molecular species gives the distribution of their internal accessible volume among pores of different sizes. Thus the adsorption capacity for iodine, which is generally called the iodine number, measures the number of pores above 10 Å whereas the molasses number indicates the number of pores larger than 30 Å in diameter. A more sophisticated approach to the measurement of pore size distribution is carried out by forcing mercury under pressure into the pores of the carbon in a mercury porosimeter, while a complete characterization involves gas adsorption and calorimetric measurements as described later in this book. Typical values of some of the properties used to characterize activated carbons are given in Table 1 of Chapter 1.

This book is divided into six chapters covering manufacture, surface structure (which includes chemical as well as porous structure), surface characterization, surface modifications, and applications of active carbons. The various factors involved in the manufacture of activated carbons using several raw materials are closely guarded secrets. Chapter 1 thus describes the basic steps involved in the manufacture of active carbons, the selectivity and suitability of different raw materials, and the probable mechanisms of the physical and chemical activation processes.

The surface structure of the activated carbons is discussed in two chapters. Chapter 2 deals with the chemical structure, presenting a comprehensive survey of the nature and the characteristics of the carbon–oxygen surface structures, the physical, chemical, and physicochemical methods of their measurements, which include ESCA (XPS), and the latest innovations in infrared spectroscopy. The surface chemistry of basic carbons has also been included. The porous structure of active carbons briefly describes the classification of pores, their characterization and contribution to surface area, distinction between internal and external surfaces, and their contribution to the adsorption of gases and vapors. A brief description of various theories dealing with physical adsorption, and the thermodynamic consequences of the Dubinin's micropore volume theory are also discussed in Chapter 3.

The characterization of active carbons by immersion calorimetry, adsorption of polar and nonpolar vapors, and adsorption from solutions are considered in Chapter 4. The importance of active surface area, its measurement, and measurement of active sites and their characterization are also discussed.

The modification of active carbons by surface impregnation, halogenation, nitrogenation, and sulfurization are dealt with in Chapter 5. The influence of different types of surface structures (surface complexes) on the surface characteristics and surface behavior of carbons is discussed.

Chapter 6 describes some applications of active carbons. The factors involved in the application of active carbons for the removal of organics and inorganics from the aqueous phase are delineated. The use of activated carbon for the recovery of gold and silver from their cyanide solution is discussed and the various theories of gold recovery are reviewed. The possibility of using active carbon as a catalyst for certain oxidation, combination, decomposition, halogenation, and dehalogenation reactions is also discussed.

Contents

in vacuum and by oxidation with nitric acid. The presence of acidic oxygen enhanced the preference for the more polar component of the solution and its removal enhanced the preference for the less polar component. These workers suggested that in addition to these polar and nonpolar interactions, the adsorption from solutions may also be influenced by energetic inhomogeneities of the carbon surface, which include defects, unsaturated sites, and free radicals.

Certain departures from the usual composite isotherm shapes have also been observed. Puri and co-workers studied the adsorption on Spheron-6 from ethylene glycol—water solutions in which both the components were polar in character. The isotherms were U shaped. The isotherm on the oxygen-free Spheron-6 showed one peak, whereas that on the oxygen-containing Spheron-6 showed two distinct peaks (Fig. 31). The composite isotherms with two peaks were termed "stepped isotherms" by Kipling et al. (72,122). When the two linear regions were extrapolated to zero concentration, the amounts adsorbed were found to be in the ratio of 1:2, indicating the possibility of the formation of a second layer.

4.4 ACTIVE SITES IN CARBONS

Active carbons have a stucture consisting of sheets of aromatic condensed ring systems stacked in nonpolar layers. These sheets have limited dimensions and therefore present edges. In addition, these sheets are associated with defects, dislocations, and discontinuities. The carbon atoms at these places have unpaired electrons and residual valencies and are richer in potential energy. Consequently, these carbon atoms are highly reactive and constitute active sites or active centers. A considerable amount of research has been aimed at understanding the number and nature of these active sites in view of the surface and catalytic reactions of carbons. Since the tendency of carbons to chemisorb oxygen is greater than their tendency to chemisorb any other species, much of our understanding of these active sites comes from the chemisorption of oxygen.

The first suggestion that the carbons are associated with different types of active sites came from the work of Rideal and Wright (123) on the oxidation of carbon surfaces with oxygen gas. These workers suggested three different types of sites which behaved differently at different oxygen pressures. The rates of oxygen chemisorption at 200°C were different at the three types of sites. Allardice (124), while studying the kinetics of chemisorption of oxygen on brown charcoal at temperatures between 25 and 300°C in the pressure range 100—700 torr, observed a two-step adsorption, which he attributed to the presence of two different types of sites. Dietz and McFarlane (125), while studying the adsorption of oxygen

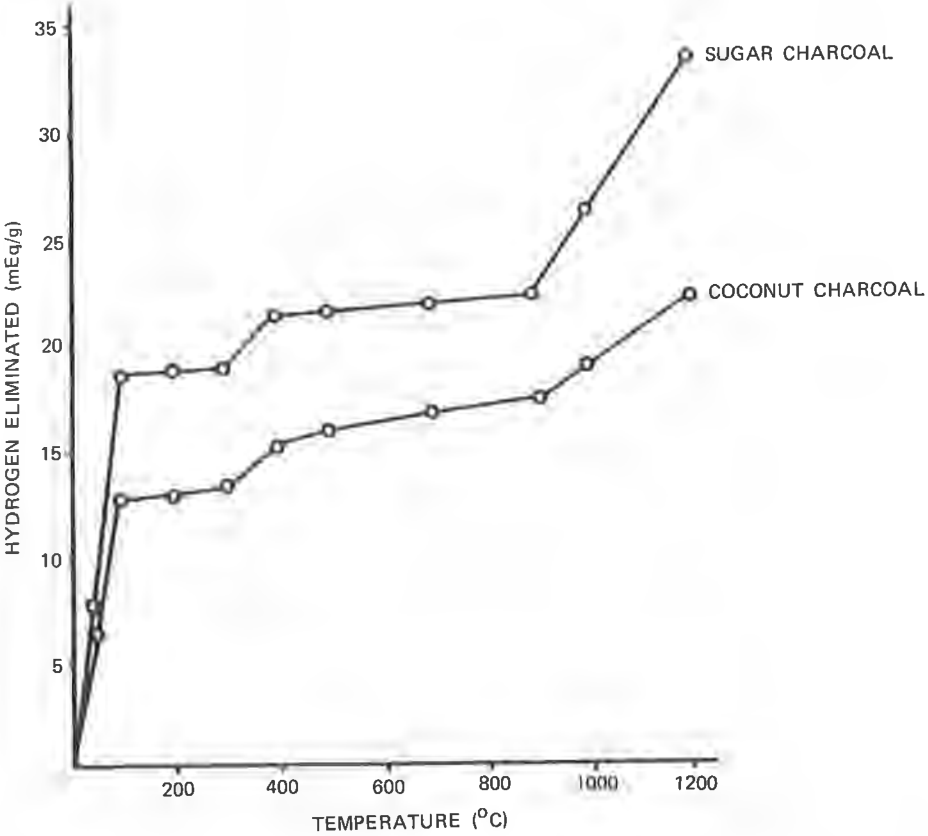

Figure 32 Elimination of chemisorbed hydrogen from charcoals by chloridation at different temperatures. [From Puri and Bansal (128a).]

on evaporated carbon films of high surface area at temperatures between 100 and 300°C and at oxygen pressures of the order of 100 millitorr, observed a rapid initial adsorption followed by a much slower adsorption. Carpenter and co-workers (126,127), during the intial stages of oxidation of different varieties of coals at temperatures of 65, 85, and 105°C, found that the chemisorption of oxygen obeyed the Elovich equation only in the first 5-min period. As the time period of oxidation increased, the quantity of oxygen chemisorbed exceeded the amounts predicted by the Elovich equation. This was attributed to the creation of fresh adsorption sites by the desorption of oxidation products such as CO_2, CO, and H_2O. Puri and Bansal (128,128a), while studying the chlorination of sugar and coconut

Table 23 Chemisorption of Oxygen on Activated Graphon at Different Temperatures

Experiment using the same sample	2.9% burnoff		19.9% burnoff	
	Temperature of chemisorption (C°)	Chemisorption capacity (μmol/g)	Temperature of chemisorption (C°)	Chemisorption capacity (μmol/g)
1	300	16.6	300	54.4
2	400	18.6	300	55.3
3	450	27.6	500	120.1
4	500	44.2	300	60.5
5	300	16.8	550	180.6
6	500	49.1	300	112.0

Source: Lussow et al. (129).

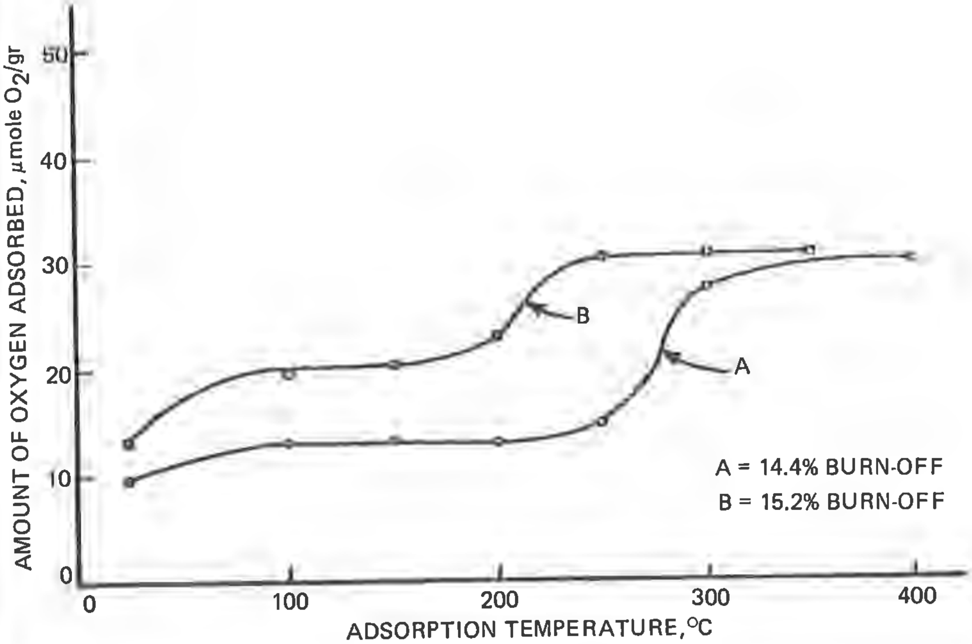

Figure 33 Saturation amounts of chemisorbed oxygen on activated graphon at different temperatures. [From Hart et al. (130).]

charcoals at different temperature between 30 and 1200°C, observed that the chemisorbed hydrogen was eliminated in a number of steps depending on the temperature of the treatment (Fig. 32). This was attributed to the fact that hydrogen in charcoals was bonded at different types of sites associated with varying energies of activation.

Lussow et al. (129) studied the kinetics of chemisorption of oxygen on graphon activated to eight different burnoffs between 0 and 35% in the temperature range of 450–675°C. The activated graphon samples were cleaned by evacuation at 950°C in a vacuum of 10^{-5} torr before chemisorbing oxygen. The saturation amounts of oxygen increased sharply at temperatures above 400°C, the amounts being almost two to three times greater. The adsorption of oxygen at 300°C after the first chemisorption at 500°C (Table 23) showed that the additional amount of chemisorption at temperatures above 400°C was not due to any additional activation of the graphon caused by the chemisorption above 400°C. It was also found that when the pressure of oxygen was increased from 0.5 to 700 torr the amount of oxygen chemisorbed was almost doubled. These results clearly

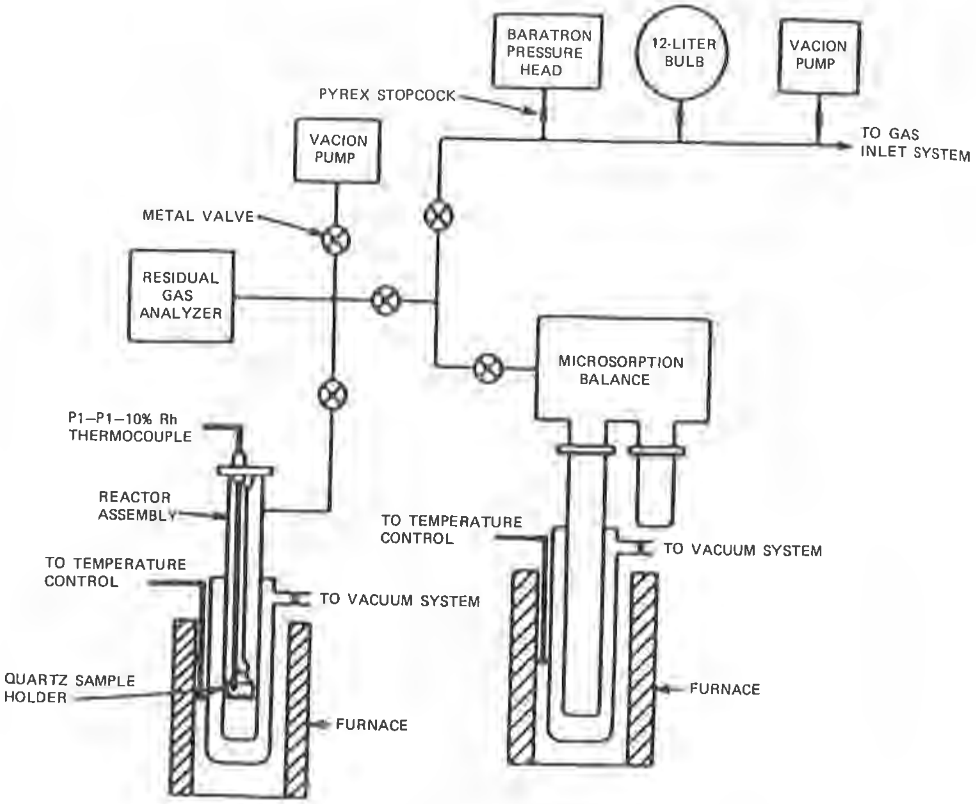

Figure 34 Schematic of ultraclean vacuum system for study of chemisorption of oxygen. [From Bansal et al. (132).]

showed that more than one type of site existed on the activated graphon surface. Hart et al. (130,131), while studying the rates of oxygen chemisorption on activated graphon (14.4% burnoff) in the temperature range 300–625°C at an oxygen pressure up to 0.5 torr using a mass spectrometer, observed two different rates of adsorption, one below and the other above 250°C. When the chemisorption at 300°C was studied for short time intervals, the saturation value was found to correspond to the value obtained below 250°C. However, when the adsorption was continued for longer periods another saturation value was obtained. This sharp increase in the saturation amount of oxygen at temperature above 250°C or at longer time intervals was attributed to the presence of two types of sites, which differed in their activation energies of adsorption (Fig. 33). The activation energy of adsorption at relatively more active sites was found to be 7.4 kcal/mol. The maximum amount of oxygen chemisorbed on these sites was estimated to occupy 2.8 m^2/g or about 2.6% of the BET surface area.

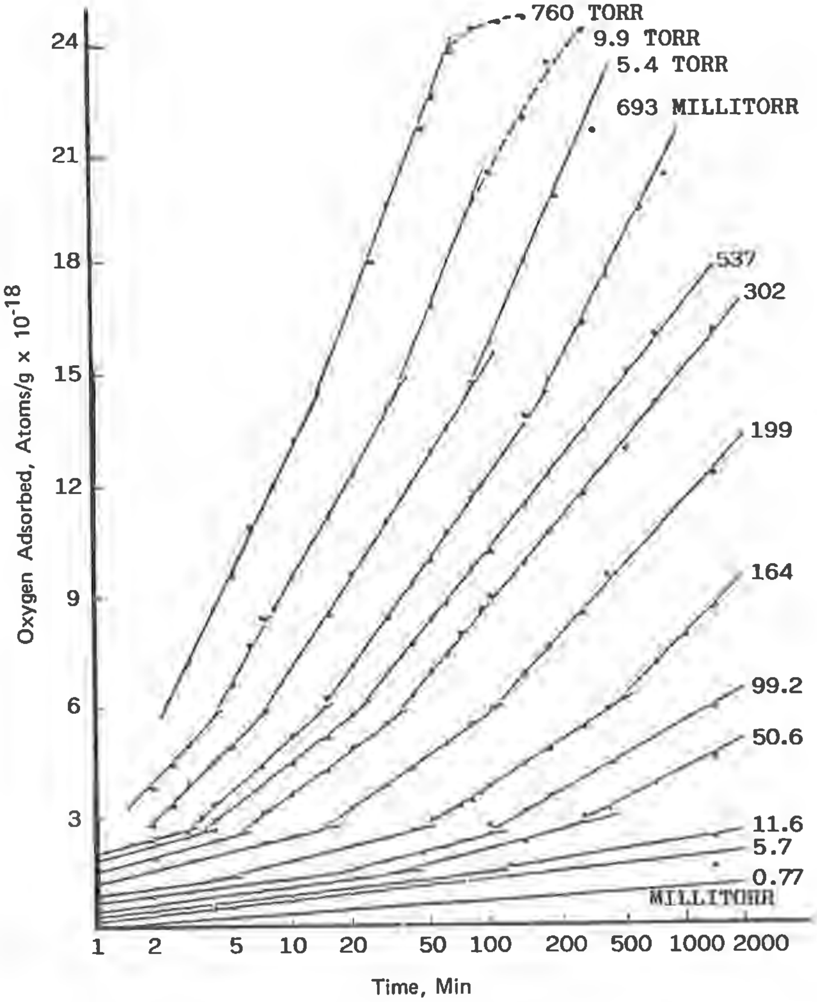

Figure 35 Elovitch plots of oxygen chemisorption on graphon at different pressures and temperatures. [From Walker et al. (133).]

Table 24 Instantaneous Adsorption Rates Calculated Midway in Each Linear Region; Rates Normalized with Respect to Pressure

Pressure (mtorr)	Rate (atoms/g · min · mtorr)				
	I ($Q = 0.6 \times 10^{18}$)	II ($q = 1.8 \times 10^{18}$)	III ($q = 4.5 \times 10^{18}$)	IV ($q = 9.6 \times 10^{18}$)	V ($q = 18.0 \times 10^{18}$)
0.77	2.1×10^{15}	—	—	—	—
5.76	2.5	—	—	—	—
11.6	2.7	—	—	—	—
22.9	2.0	2.6×10^{14}	—	—	—
50.6	2.0	2.9	—	—	—
99.2	—	2.9	—	—	—
164	—	3.0	—	—	—
199	—	4.0	2.2×10^{14}		
302	—	3.9	2.0	5.2×10^{13}	—
537	—	—	2.2	6.5	—
693	—	—	2.3	6.9	8.7×10^{12}
5438	—	—	2.0	4.5	7.6
9930	—	—	2.0	4.9	8.9
760×10^3	—	—	—	1.0	3.1

Source: Walker et al. (133).

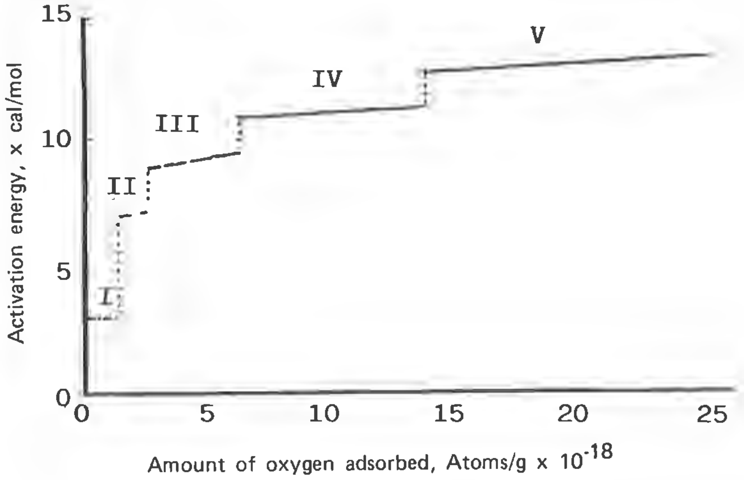

Figure 36 Variation of activation energy as a function of oxygen chemisorption on activated graphon. [From Bansal et al. (132).]

Bansal and colleagues (132–134) characterized ultraclean surfaces of graphon by studying the kinetics of chemisorption at low temperatures in the range 70–160°C and at oxygen pressures between 7.7×10^{-4} and 760 torr. The activated graphon sample (16.6% burnoff) was cleaned by heat treatment at 1000°C in a vacuum of the order of 10^{-9} torr. The apparatus used for cleaning the graphon sample and for studying chemisorption kinetics was a stainless steel system that conformed to all the requirements of an ultraclean system. The apparatus essentially consisted of a gas inlet system; a vacuum assembly, which contained a vacion pump; and an adsorption unit, which included a baratron differential manometer, a residual gas analyzer, and a Cahn microsorption balance (Fig. 34).

The results of these kinetic measurements when plotted according to the Elovich equation (q vs. log t) showed linear regions; the number of linear regions and the time of appearance of a linear region depended on the initial oxygen pressure or the temperature of the adsorption (Fig. 35). For example, the plots showed only one linear region at oxygen pressures lower than 10 mtorr and two linear regions between 50 and 683 mtorr pressure and at adsorption temperatures between 0 and 125°C. The number of these linear regions decreased at higher pressures or at higher temperatures. The instantaneous rates of adsorption calculated midway in each linear region when normalised with respect to oxygen pressure were found essentially proportional to the first power of oxygen pressure,

Table 25 Comparison of Experimental and Theoretical Values of Activation Energy for Chemisorption of Hydrogen on Graphite

Experimental		Theoretical	
Site	*E* (kcal/mol)	C—C distance (nm)	*E* (kcal/mol)
I	5.7	0.362	9
II	8.3	0.335	11
III	18.4	0.284	19
IV	30.4	0.246	28
V	—	0.142	50

Source: Bansal et al. (134).

which was varied widely, Furthermore, the rate of oxygen chemisorption decreased sharply in advancing from stage I to stage V (Table 24), where it was 250-fold less than that for stage I. These linear regions were thus postulated to represent different kinetic stages of the same chemisorption process involving adsorption at different types of sites. This received further support from the fact that each of the kinetic stages appeared after the adsorption of a definite amount of oxygen, although the time and the temperature of appearance and the temporal range of existence of any particular kinetic stage was determined by the initial pressure of the gas or the temperature of adsorption. In general, any stage appeared earlier and lasted for a shorter time as the pressure or the temperature was increased. A lower kinetic stage disappeared almost completely at higher pressures or at higher temperatures because the rates of adsorption were so rapid that the lower kinetic stage passed in the time period between the exposure of the carbon to the gas and the first measurement, so that the amounts adsorbed under these conditions in the very first measurement were larger than the amounts chemisorbed in the lower stages of adsorption. The activation energies of adsorption calculated from the Arrhenius plots of instantaneous rates at different coverages were found to be independent of surface coverage on any one group of sites, although the activation energies were different for adsorption on different groups of sites (Fig. 36). In all, five different groups of sites were observed in these studies. The activation energies varied between 3.1 and 12.4 kcal/mol as the chemisorption proceeded from the most active to the least active sites. Bansal et al. (134) also studied the kinetics of chemisorption of hydrogen on the same sample of activated graphon as a function of hydrogen pressure and adsorption temperature. The rates of hydrogen chemisorption were very low compared to those of oxygen. Only four types of active sites could be observed with an adsorption temperature of 600°C. Chemisorption experiments were not carried out at higher temperatures because the graphon surface showed burning, producing gaseous species which vitiated the kinetic measurements.

The existence of these discrete types of sites has been attributed to the difference in the geometrical arrangement of the surface carbon atoms (132–134). As the carbon surface presents several carbon–carbon distances to the incoming gas molecules, the activated complex formed between the gas atoms and the two surface carbon atoms would be expected to have different potential energy configurations, depending on these spacings between the carbon atoms, resulting in a variation of the activation energies of chemisorption. Sherman and Eyring (135) made theoretical calculations of the energy of activation for dissociative chemisorption of hydrogen on a carbon surface and found the values to vary with the carbon–carbon spacings. A comparison of the theoretical values of Sherman and Eyring (135) and the experimental values obtained by Bansal et al. (134) is given in Table 25. The carbon–carbon distances selected in this table are those which the hydrogen molecule would most likely enounter when approaching the carbon surface. The spacing 0.246 nm represents the configuration terminating in $(10\bar{1}\ 1)$ face, the spacings 0.142 and 0.284 nm for $(11\bar{2}\ 1)$ termination, and the spacings of 0.335 and 0.362 nm for distances between edge carbon atoms in adjacent basal planes. Agreement between the experimental and the theoretical values supports the concept that these carbon spacings act like discrete types of sites on which the chemisorption of gases generally can occur.

Puri et al. (136–138) obtained fairly convincing evidence for the presence of certain highly active sites of an entirely different kind, which they called unsaturated sites. These unsaturated sites can be determined by interacting carbons with the aqueous solution of bromine in potassium bromide. These sites are produced when carbons associated with oxygen are outgassed at high temperatures, the optimum temperature being between 600 and 700°C. The concentration of these sites was shown to vary with the combined oxygen which comes off as carbon dioxide (Table 26). One mole of unsaturated sites was created by the chemisorption of two moles of oxygen as carbon dioxide.

The concentration of the active sites on a carbon surface has been measured in terms of the active surface area (ASA) by Laine and co-workers (139–141). The active surface, according to these workers, is an index of the reactivity of a carbon surface and can be determined from the amount of oxygen chemisorbed at 300°C in

Table 26 Active Sites as Determined by Bromine Adsorption from Aqueous Solutions by Carbons

Carbon	Sugar charcoal		Cotton stalk charcoal	
	Unsaturated active sites (mmol/g)	Decrease in CO_2-complex (mmol/g)	Unsaturated active sites (mmol/g)	Decrease in CO_2-complex (mmol/g)
Original	—	—	—	—
Outgassed at				
300°	0.80	1.69	0.27	0.56
400°	1.34	2.59	0.49	1.06
500°	1.62	3.31	0.67	1.41
700°	1.85	3.63	0.89	1.69
900°	1.83	3.63	0.88	1.69
1000°	1.87	3.70	0.86	1.65
1200°	1.85	3.64	0.89	1.69

Source: Puri et al. (136).

Table 27 Comparison of Active Surface Area Calculated by Chemisorption of Oxygen at 300°C and the Most Active Site Area Obtained from Chemisorption at Higher Temperatures

Burnoff (%)	ASA (Laine method) (μmol O/g)	Most active site area (μmol O/g)
0	5.0	5.0
0	4.4	53.9
3.3	17.8	40.4
6.4	27.6	27.6
7.7	30.9	28.8
14.4	44.4	45.2
14.4	44.4	45.2
14.4	44.4	44.8
14.4	44.4	50.3
18.5	52.0	49.5
18.5	52.0	47.8
18.5	52.0	48.2
18.5	52.0	50.4
18.5	52.0	46.0
18.5	52.0	50.2
18.5	52.0	47.0
18.0	52.0	50.7
18.5	52.0	52.7
18.5	52.0	53.4
19.9	54.4	50.0
25.8	65.0	64.6
25.8	65.0	65.0
34.9	82.0	76.0

Source: Lussow et al. (129).

24 hr at an initial oxygen pressure of 0.5 torr. Assuming that one oxygen atom is adsorbed at each carbon atom and that each carbon atom occupies an area of 0.083 nm^2, the oxygen chemisorbed can be converted into active surface area. These workers activated graphon to seven different burnoffs in order to create varying amounts of active surface and observed that ASA increased with the degree of burnoff and could be related to the reactivity of the graphon toward oxygen. However, in later work (129,130) on the chemisorption of oxygen at higher temperatures between 300 and 675°C, they observed that there existed more than one type of active site which differed in reactivities toward oxygen. The rate of chemisorption of oxygen on the less active sites was not appreciable at low oxygen pressures until the chemisorption temperature was 400°C or above. Consequently they suggested that Laine's method, which involved chemisorption at 300°C, determined only the surface area covered by the most active groups of active sites. These workers (129) calculated the area covered by the most active group of sites from the low coverage part of the reactivity data, when the reactivity of the less active sites was supposedly negligible, and found the values to be in good agreement with Laine's values (Table 27). Thus these workers pointed out the necessity of obtaining reactivity data under proper conditions to ensure that the observed reactivity was not being unduly influenced by the reaction on less active sites.

Hoffman et al. (142), while studying the chemisorption of several hydrocarbons (e.g., propylene, ethylene, propane) and methane on activated graphon, observed that the adsorption of each hydrocarbon increased with burnoff due to increase in the active surface area ASA of the graphon. However, the ASA covered by these hydrocarbons was much less compared to the ASA covered by oxygen at all degrees of burnoff (Table 28). Furthermore, propylene covered a larger ASA compared to ethylene or methane or *n*-butane. This may be attributed partly to the larger size of these hydrocarbon molecules, which, when adsorbed on an active site, are likely to shield some of the neighboring sites to make them unavailable for adsorption. Thus ASA has a meaning only with respect to the chemisorption of a particular species. Whereas Laine's ASA can measure reactivity toward oxygen, it fails to measure the reactivity of the graphon toward these hydrocarbons.

Dentzer et al. (143) examined the adorption and decomposition of silver diamine complexes from ammoniacal solutions on a graphitized carbon black, Vulcan 3, activated to different degrees of burnoff. These workers observed that the amount of silver adsorbed increased with increase in the degree of burnoff. A linear relationship (Fig. 37) was observed between the amount of silver adsorbed and the ASA as determined by Laine's method. This was attributed to

Table 28 Active Surface Area Occupied by the Chemisorption of Different Gases on Graphon at 300°C

	Burnoff (%)						
Sample	723 K	1223 K	Total	Oxygen ASA (m^2/g)	Propylene (ASA (m^2/g)	Ethylene ASA (m^2/g)	*n*-Butane ASA (m^2/g)
1	0	0	0	0.264	0.056	0.033	0.012
2	0	0.61	0.61	0.94	0.44	0.32	0.18
3	4.9	0.85	5.75	2.25	1.06	0.72	0.46
4	24.1	0.40	24.5	5.00	1.89	0.19	0.87

Source: Hoffman et al. (142).

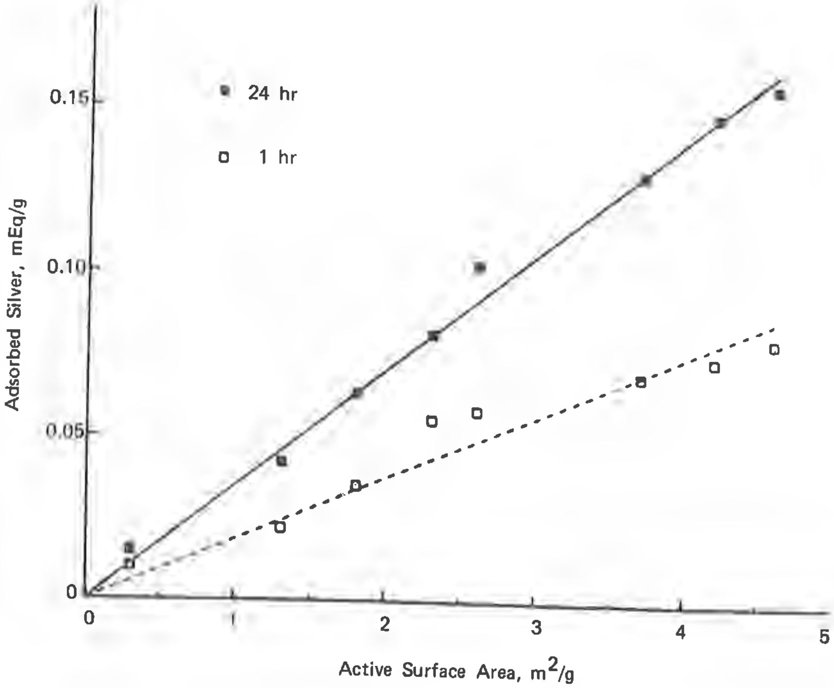

Figure 37 Amount of silver adsorbed in relation to active surface area of carbons. [From Dentzer et al. (143).]

the specific reductive interaction of the silver diamine with the carbon-active sites producing metallic silver, which was chemisorbed on the active sites.

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5

Surface Modification of Carbons

Carbons are almost invariably associated with appreciable amounts of oxygen. The oxygen is chemisorbed even on mere exposure to air or oxygen preferably at 400–500°C. The oxygen is fixed firmly and comes off only as oxides of carbon on high-temperature heat treatment in vacuum or in an inert atmosphere. Similarly, it is well known that all microcrystalline carbons contain chemically bonded hydrogen, the amount depending on the history of its formation. The hydrogen is held so firmly that it is not given off completely even on outgassing at 1200°C. These carbons can also fix nitrogen on treatment with ammonia; sulfur on treatment with hydrogen sulfide, carbon disulfide, or sulfur; chlorine on treatment with the gas; and bromine on treatment in the gaseous or solution phase. These treatments give rise to stable carbon–nitrogen, carbon–sulfur, carbon–chlorine, or carbon–bromine surface structures (surface compounds) respectively. There is also evidence that the carbons can adsorb certain molecular species such as phenols, amines, nitrobenzene, surfactants, and several other cationic species.

X-ray diffraction studies have shown that these heteroatoms or molecular species are bonded or retained at the edges and corners of the aromatic sheets or to carbon atoms in defect positions of the aromatic sheets, or they can be incorporated within the carbon layer, forming heterocyclic ring systems. These carbon atoms have unsaturated valencies and have a tendency to reduce their potential energy by forming bonds with these heteroatoms. Since these edges constitute the main adsorbing surface, the presence of these heteroatoms or molecular species is expected to modify the surface characteristics and surface behavior of these carbons. Similar surface compounds in carbon blacks determine their application in the rubber, plastic, and paint industries and they determine the lubricating properties in graphites as well as their use as moderators in atomic reactors. In the case of carbon fibers these very surface compounds determine their adhesion to plastic matrices and consequently determine their use in composites.

5.1 MODIFICATION OF CARBONS BY OXIDATION

Carbons are always associated with varying amounts of chemisorbed oxygen unless special care is taken to eliminate it. In fact this combined oxygen has often been found to be the source of the property by which a carbon becomes useful or effective in certain respects. Carbons also have a great tendency to extend this layer of bonded oxygen by chemisorbing oxygen, and many of their reactions arise because of this tendency. For example, carbons are capable of decomposing oxidizing gases such as ozone (1–4), oxides of nitrogen (5,6) chemisorbing oxygen in each case. They also decompose aqueous solutions of silver salts (7), halogens (8–10), ferric chloride (11), potassium and ammonium persulfates (12–13), sodium hypochlorite (14,15), potassium permanganate (16,17), potassium dichromate (17), sodium thiosulfate (18), hydrogen peroxide (19,20), and nitric acid (17,21,22). In each case there is chemisorption of oxygen and a buildup of the oxide layer on the carbon surface.

Carbons can also be oxidized by heat treatment in air, carbon dioxide, or oxygen. The nature and the amount of surface oxides formed on treatment with oxygen depends on the nature of the carbon and the history of its formation, its surface area, and the temperature of treatment. The reaction of carbons with oxygen can proceed in several ways depending on the temperature at which the reaction is carried out:

$$\underset{\text{surface compound}}{C + O \longrightarrow C(O)} \quad \text{formation of oxygen surface compound}$$

$$C + O \longrightarrow CO + CO_2 \quad \text{gasification}$$

$$C(O) \longrightarrow CO + CO_2 \quad \text{decomposition of surface compound}$$

At temperatures below 400°C, the chemisorption of oxygen and formation of the carbon–oxygen surface compounds dominate, whereas at temperatures above 400°C, the decomposition of the surface compounds and the gasification of the carbon are the dominating reactions. In case of oxidative treatments in solutions, the major reaction is the formation of the surface compounds, although some gasification may also occur depending on the strength of the oxidative treatment and the severity of the experimental conditions. The formation of the surface oxygen compounds using various types of carbon and using different oxidative treatments in gaseous and liquid phases has been studied by a large number of investigators and has been well reviewed (23–25). Thus we do not discuss this aspect in detail, but merely say that carbons have a tendency to pick up oxygen at least to some extent under all conditions when in contact with an oxidative reagent.

As mentioned earlier, the oxygen in carbons is present at sites which are generally responsible for their adsorption characteristics, surface reactions, and surface behavior. Thus its presence will greatly modify the surface properties of carbons. In fact it is assumed that most of the properties of carbons are the properties of these oxygen structures. Consequently, their influence on carbon surface behavior is felt and discussed in almost every chapter of the book in one form or another. We therefore do not discuss the modification of carbons by these surface compounds separately in this chapter.

5.2 MODIFICATION OF ACTIVE CARBONS BY SURFACE IMPREGNATION

The impregnation of carbons at once brings to mind the impregnation by metals, a subject that has been widely studied and extensively reviewed because of its importance in heterogeneous catalysis. Metals and their oxides, dispersed as small particles on high surface area carbons and other supports, have been used widely and are being used as catalysts for various industrial applications. The primary role of the carbon support is to favor the formation of a highly dispersed metal phase and to physically separate the metal crystallites, thus increasing their stability on sintering. The study of supported small metal crystallites started in the late 1970s and has grown significantly since. The impregnation of metals in carbonaceous materials also modifies the gasification characteristics and varies the porous structure of the final carbon product. Thus the procedure has been applied to obtain carbons with a given microporous structure. The subject of this section, however, is not these developments but a study of the modification of the surface behavior and adsorption characteristics of carbons by chemical reagents which are present as a part of the adsorbed phase.

Activated carbons impregnated with potassium iodide and similar compounds (26) and with amines (27,28) including several pyridines have been widely used in the nuclear industry for the retention of radioactive iodine compounds from coolant release and ventilation systems. These carbons are required to remove very low levels of iodine and its compounds with high efficiency from gas streams, which in some cases could be of very high humidity. The performance of a carbon has been found to vary with manufacture and by aging. Billinge et al. (26) compared the efficiency of potassium iodide–impregnated coconut and coal-based charcoals for trapping radioactive methyl iodide from gas-cooled nuclear reactors. The coal-based impregnated charcoal was better than the impregnated coconut charcoal, which in turn was better than the impregnated activated charcoal. The trapping of methyl iodide was related to the associated oxygen in carbons. The oxygen evolved as carbon dioxide on outgassing reduced the retention efficiency more than the oxygen evolved as carbon monoxide. The impregnated potassium iodide reacted with the oxygen groups on carbons and modified their desorption behavior, thereby improving the efficiency to retain radioactive methyl iodide.

Impregnation with pyridine and picoline has been used as a treatment to keep ASC Whetlerites from degrading in the presence of moisture (29). Activated carbons impregnated with Cu^{2+}, Ag^{+}, Cr^{6+}, NH^{4+}, and CO_3^{2-} were found to be efficient adsorbates for arsene, hydrogen cyanide, cynogen chloride, chloroform, and phosgene. Baker and Poziomek (27) modified adsorptive properties of coal-based active carbons by impregnating them with pyridine, 4-vinylpyridine, 4-aminopyridine, 4-cynopyridine, and 4-*n*-propylpyridine. The carbons were impregnated by volatile impregnants in a rotary evaporator and the amounts impregnated determined by the difference between the initial and the final weight of the carbon. The nonvolatile impregnants were adsorbed on the carbon surface from alcohol solutions. The adsorption capacity of the impregnated charcoals were compared for carbon tetrachloride and cynogen chloride under dynamic conditions and for methyl iodide under equilibrium conditions.

Impregnation of a small percentage of pyridines decreased the adsorption of carbon tetrachloride by a small percentage (Table 1). Increasing amounts of impregnants decreased the adsorption of carbon tetrachloride. In the case of cynogen chloride, the reactivity of the carbons increased with increase in the amount of a given impregnant. The reactivity, however, varied from one pyridine to another but not necessarily in the order of their expected neucleophilicities or basicities (Table 2). The reactivity of the charcoals impregnated with the five pyridines toward methyl iodide did not parallel their reactivity toward cynogen chloride but was rather in the following order:

Pyridine > 4-vinylpyridine > 4-aminopyridine >
4-cynopyridine > 4-*n*-propylpyridine

(Table 2). When the same charcoal sample was impregnated with 4-aminopyridine and 4-vinylpyridine to different degrees, the retention of methyl iodide increased (from 53 to 75%) with increase in the

Table 1 Influence of Impregnation of Carbon on the Relative Adsorption of Carbon Tetrachloride

Impregnant	Loading (mmol/g)	Relative CCl_4 adsorption (%)
None	0	100
Pyridine	0.253	96
4-Cyanopyridine	0.192	95
4-Vinylpyridine	0.190	93

Source: Baker and Poziomek (27). Reproduced with permission from Pergamon Press.

concentration of 4-aminopyridine on the surface of the carbon but remained more or less unchanged (around 71%) with increase in the concentration of 4-vinylpyridine on the carbon surface (Table 3).

Baker and Poziomek (27) observed that the charcoal impregnated with 4-vinylpyridine showed different behavior in many respects. First, it showed higher adsorption of cynogen chloride (0.605 mmol/g) compared to pyridine-impregnated charcoal (0.482 mmol/g), although 4-vinylpyridine is less basic than pyridine. Second, the 4-vinylpyridine-impregnated charcoal failed to result in any weight loss on heating at 150°C under 3 torr pressure for many hours compared to a 5% weight loss in the case of 4-*n*-propylpyridine (which has a boiling point similar to that of 4-vinylpyridine). Third, 4-vinylpyridine could be removed from the charcoal surface only to the extent of 66% against 86% for *n*-propylpyridine when subjected to soxhlet extraction with ethanol for 6 hr. On the basis of this evidence, these workers (27) suggested that 4-vinylpyridine undergoes adsorption polymerization when adsorbed on activated charcoal. To further substantiate their views these workers studied the adsorption of cynogen chloride on an active carbon impregnated with poly-4-vinylpyridine. This sample adsorbed 0.073 mmol CNCl/g, which was comparable with the control carbon sample (0.085 mmol/CNCl/g), indicating that the nitrogens of the polymer were not available for reaction with cynogen chloride. This contrasted sharply with the results of cynogen chloride adsorption on the carbon sample impregnated with 4-vinylpyridine (0.200 mmol CNCl/g), which indicated that the nitrogens of the adsorption polymer were available for reaction. The 4-vinylpyridine–impregnated carbon could adsorb only two-thirds of the amount of water adsorbed by activated carbon or any of the other impregnated carbons.

Table 2 Influence of Impregnation of Carbon on the Adsorption of Cynogen Chloride

Impregnant	Amount impregnated (mmol/100 g)	Saturation adsorption capacity for $CNCl_3$ (mmol/100 g)	Ratio of additional CNCl adsorbed to impregnant (mmol)
None	0	85	0
4-Aminopyridine	212	272	0.882
Pyridine	253	207	0.482
4-Vinylpyridine	190	200	0.605

Source: Baker and Poziomek (27). Reproduced with permission from Pergamon Press.

Table 3 Influence of Impregnation of Charcoal on the Retention of Methyl Iodide

Impregnant	Concentration of impregnant (mmol/g)	Methyl iodide retained (%)
4-Vinylpyridine	0.048	76.5
	0.096	73.3
	0.190	71.3
	0.286	77.0
	0.475	77.7
4-Aminopyridine	0.053	53.5
	0.106	57.5
	0.212	61.7
	0.318	69.2
	0.530	75.5
Pyridine	0.253[a]	80.2
4-Cynopyridine	0.192[a]	54.8
4-*n*-Propylpyridine	0.165[a]	48.7
4-Vinylpyridine	0.190[a]	71.3
4-Aminopyridine	0.212[a]	61.7

[a] Corresponds to a 2% by weight loading on the charcoal.
Source: Baker and Poziomek (27). Reproduced with permission from Pergamon Press.

Barnir and Aharoni (30) compared the adsorption of cynogen chloride on active carbon before and after impregnation with Cu^{2+}, Cr^{6+}, Ag^{+}, and NH_3 in a given ratio. The adsorption of cynogen chloride, which was reversible in the case of active carbon, became irreversible after impregnation, although the adsorption capacity did not show any increase. Thus whereas cynogen chloride was the main gas evolved on heating the active carbon treated with cynogen chloride, carbon dioxide was mainly desorbed from the impregnated charcoal. The presence of moisture in the carbon also hindered the desorption of cynogen chloride and enhanced the desorption of carbon dioxide. It was postulated that the cynogen chloride was adsorbed both physically and chemically on the surface of the carbon as well as on the additive (impregnant) surface. The cynogen chloride chemisorbed on the impregnant surface reacted faster with water sorbed on the carbon or linked with the impregnating material producing carbon dioxide and ammonium chloride:

$$CNCl + 2H_2O \rightarrow CO_2 + NH_4Cl$$

This process regenerated the surface of the impregnant where more cynogen chloride could be chemisorbed.

Reucroft and Chion (31,32) compared the adsorption behavior of BPL-activated carbon with ASC Whetlerite (obtained by impregnating BPL-activated carbon with Cu^{2+}, $CrO_4{}^{2-}$, and Ag^{+}) and ASB carbons (prepared by impregnating BPL with Cu^{2+} and BO_3^- in different mole ratios) for chloroform, phosgene, cynogen chloride, and hydrogen cyanide using a gravimetric adsorption system. The adsorption isotherms were analyzed in terms of the Dubinin—Polanyi equation. A comparison of the affinity coefficients (β_{ex}) calculated from the slopes of the experimental isotherms with theoretical values (β_{th}) for adsorption of chloroform and phosgene (Table 4) showed about 17% higher adsorption than predicted on a theoretical basis for all carbons except ASC Whetlerite—impregnated carbons. In the case of the latter carbon the isotherm was not linear in the low-pressure region and consequently (β_{ex}) and (β_{th}) for adsorption of cynogen chloride for the BPL and impregnated BPL—activated carbon (Table 5) were about 20% higher than predicted for each of the three ASB-impregnated carbons. The ASC Whetlerite carbon isotherm did not obey the Dubinin—Polanyi equation and therefore the (β_{ex}) could not be obtained. The impregnation of the carbon generally lowered the micropore volume (W_0) in all cases, which was attributed to some pores being blocked or occupied by impregnating species.

The impregnated carbons showed both chemisorption and physisorption, the chemisorption being more pronounced in case of phosgene, cynogen chloride, and hydrogen cyanide on ASC and ASB carbons compred to BPL-activated carbon. Both ASC and ASB

Table 4 Adsorption Parameters of Dubinin–Polanyl Equation for Nonimpregnated and Impregnated Activated Carbons

	$\beta_{th} = 0.78$				
	$CHCl_3$ isotherm		$COCl_2$ isotherm		
Adsorbent	W_0 (cm^3/g)	$k \times 10^8$ ($cal^{-2}mol^2$)	W_0 (cm^3/g)	$k \times 10^8$ ($cal^{-2}mol^2$)	β exp $\frac{KCHCl_3}{(KCOCl_2)^{\frac{1}{2}}}$
BPL-activated carbon	0.43	2.50	0.43	3.02	0.913
ASC Whetlerite	0.35	2.90	0.36	—	—
ASB (0.1 H_3BO_3:1)	0.35	2.25	0.36	2.67	0.918
ASB (0.5 H_3BO_3:1)	0.34	2.26	0.35	2.68	0.918
ASB (1 H_3BO_3:1)	0.34	2.25	0.35	2.68	0.916
ASB (2 H_3BO_3:1)	0.32	2.27	0.32	2.67	0.922

Source: Chion and Reucroft (31). Reproduced with permission from Pergamon Press.

Table 5 Dubinin–Polanyi Adsorption Equation Parameters for Nonimpregnated and Impregnated Active Carbon

	CNCl β_{th} = 0.53			HCN β_{th} = 0.305		
Adsorbent	W_0 (cm^3/g)	$k \times 10^8$ ($cal^{-2}mol^2$)	β exp, $\frac{KCHCl_3}{(KCNCl)^{\frac{1}{2}}}$	W_0 (cm^3/g)	$k \times 10^8$ ($cal^{-2}mol^2$)	β exp, $\frac{KCHCl_3}{(KHCN)^{\frac{1}{2}}}$
BPL-activated carbon	0.42	6.11	0.640	0.42	14.9	0.410
ASC Whetlerite	0.36	—	—	0.35	—	—
ASB (0.1 H_3BO_3:1)	0.36	6.80	0.685	—	—	—
ASB (1 H_3BO_3:1)	0.35	4.71	0.691	0.14	11.4	0.444
ASB (2 H_3BO_3:1)	0.32	4.81	0.687	0.33	11.3	0.448

Source: Reucroft and Chion (32). Reproduced with permission from Pergamon Press.

carbons retained appreciable amounts of the three adsorbates after evacuation at 150°C, the amount retained being more in ASC Whetlerite. The chemisorbed amount of cynogen chloride depended on the highest initial exposure pressure of cynogen chloride, whereas the adsorption of hydrogen cyanide was almost independent of this pressure. The adsorptive capacity of these carbons decreased in the following order:

ASC Whetlerite > ASB carbons > BPL-activated carbon

This indicated that CrO_4^{2-} (or a complex form of Cr^{2-} with other ions) or Ag^+ in ASC Whetlerite produced a greater degree of chemisorptive interactions and was primarily responsible for the higher affinity toward these adsorbates. It was also found that the chemisorption increased in the order of the decreasing size of the adsorbate molecule:

Phosgene chemisorption > cynogen chloride chemisorption >
hydrogen cyanide chemisorption

for all the carbons.

The influence of temperature on the adsorption–desorption isotherms of hydrogen cyanide on BPL-activated and ASC Whetlerite–impregnated carbons was studied by Freeman et al. (33). The Dubinin–Polanyi equation gave 0.42 and 0.35 ml/g as the micropore volume for BPL and ASC Whetlerite carbons at all temperatures between 0 and 122°C. The adsorption decreased with increasing temperature for both carbons but was greater for ASC Whetlerite at lower pressures at all temperatures. This was attributed to adsorption at the active sites provided by the ionic impregnants. At higher pressure the larger surface area of the BPL-activated carbon was the dominant factor in adsorption. The Whetlerite showed chemisorption, the average value of chemisorption (0.00102 mol HCN/g C) being almost equivalent to the number of moles (0.00131 mol/g) of the impregnant, which clearly indicated that the additional adsorption at the lower pressure and the chemisorption in case of Whetlerite were due to the ionic impregnants. The heats of adsorption calculated using the Clausius–Clapeyron (Fig. 1) equation coverages at high both for BPL and Whetlerite carbons were in good agreement with the heat of liquefaction of hydrogen cyanide (≃ 6.5 kcal/mol). The heats of adsorption for the Whetlerite, however, were higher at low surface coverages, indicating chemisorption of hydrogen cyanide on the ionic impregnant sites.

The adsorption of water vapor and its binary mixtures with hydrogen cyanide on ASC Whetlerite–impregnated and BPL-activated carbons (34) showed that ASC Whetlerite adsorbed 10 times more

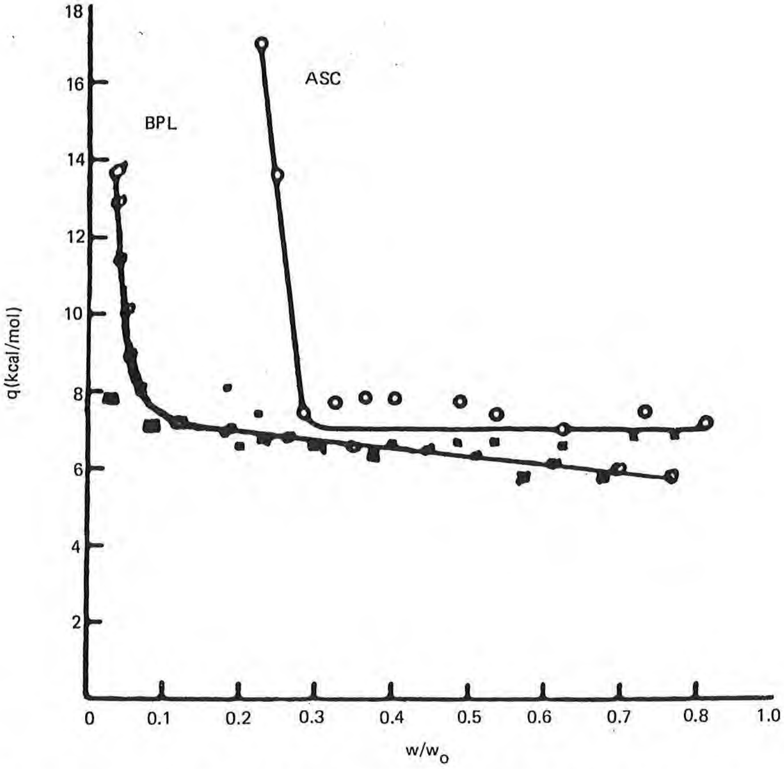

Figure 1 Isoteric heats of sorption for HCN on BPL-activated carbon and ASC Whetlerite carbon. [From Freeman et al. (33). Reproduced with permission from Pergamon Press.]

water than BPL-activated carbon at low pressures (Fig. 2), but the isotherms crossed each other at a relative pressure of about 0.7 and the saturation adsorption was more for the BPL-activated carbon. This was attributed to the adsorption being determined by the greater affinity of impregnant ions at lower relative pressures and to pore volume considerations at higher relative pressures. In ASC Whetlerite a part of the pore volume is occupied by the impregnant ions and consequently the saturation adsorption capacity is less than that for BPL-activated carbon. The adsorption of hydrogen cyanide was greater for both carbons when they had preadsorbed water and this amount exceeded the amounts of water and hydrogen cyanide

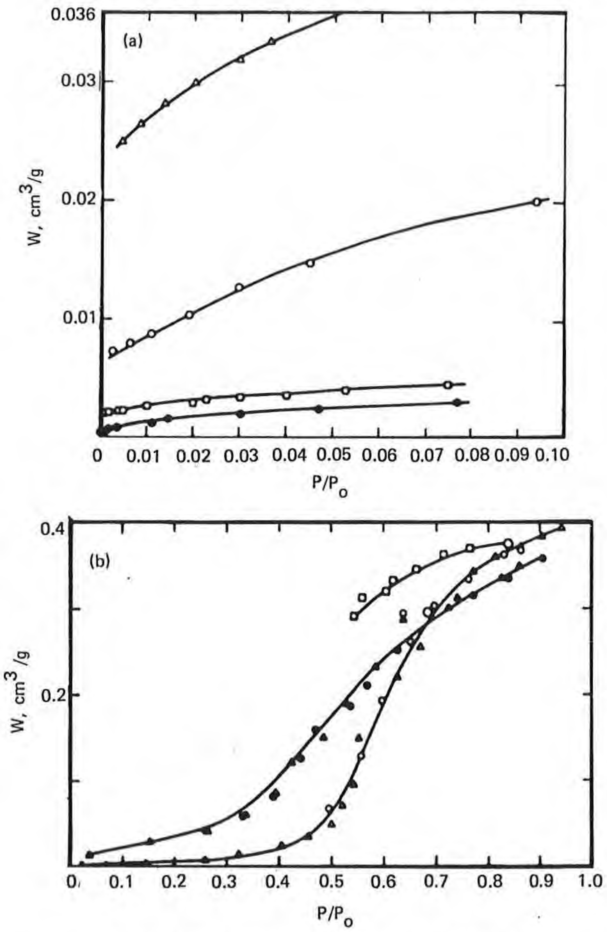

Figure 2 (a) Low pressure adsorption and desorption isotherms of water on BPL-activated and ASC Whetlerite—impregnated carbons. Open triangle, desorption of H_2O on ASC Whetlerite; open circle, adsorption of H_2O on ASC Whetlerite; open square, desorption of H_2O on BPL; closed circle, adsorption of H_2O on BPL. (b) High-pressure adsorption and desorption isotherms of water on BPL-activated and ASC Whetlerite—impregnated carbons. Open triangle, adsorption run No. 1 of H_2O on BPL; open circle, adsorption run No. 2 of H_2O on BPL; open circle, adsorption run No. 3 of H_2O on BPL; open square, desorption of H_2O on BPL; closed triangle, adsorption run No. 1 of H_2O on ASC Whetlerite; closed circle, adsorption run No. 2 of H_2O on ASC Whetlerite. [From Freeman and Reucroft (34). Reproduced with permission from Pergamon Press.]

Table 6 Adsorption Capacity of Impregnated Carbons for H_2S, SO_2, and HCN

	Weight uptake ($\mu g/cm^2$)		
Impregnant	H_2S	SO_2	HCN
None	50	220	120
$AgNO_3$	210	—	—
$Na_2CR_2O_7$	310	480	120
Cu (5%)	360	470	320
Cu (5%) + $Na_2CR_2O_7$	760	960	890

Source: Capon et al. (35).

adsorbed separately. The chemisorption of hydrogen cyanide on ASC Whetlerite was also higher in the presence of water.

An activated charcoal cloth prepared by carbonization of viscose rayon in the presence of $CNCl_2$ when impregnated with oxidizing agents such as $KMnO_4$, Na_2CR_2O, and ClO_2, with an organic tertiary amine, triethylenediamine (TEDA), and $AgNO_3$ from aqueous solutions, showed enhanced adsorption capacity (reactivity) toward low-boiling pollutant gases such as SO_2, NO_2, H_2S, HCN, and CNCl (35). The exact nature of the reaction was found to depend on the nature of the impregnant and the oxidizing agent (Table 6). The presence of $CuCl_2$ as the impregnant enhanced the adsorption capacity for all gases while the presence of organic amine (TEDA) enhanced considerably the adsorption of CNCl (Table 7). The adsorption capacity of the cloth for physically adsorbed molecules, however, was not significantly impaired after impregnation.

Jonas (36) suggested that the removal of gas or vapor from a flowing stream by a bed of chemically impregnated activated carbon granules, in which both physical adsorption and chemical reaction occur, could be represented as a series of seven consecutive steps. This sequence of steps, which is initiated when the flowing gas air stream approaches the first layer of carbon in the bed, includes mass transfer, surface diffusion, intragranular diffusion, physical adsorption, chemical reaction, and surface renewal. Jonas also deduced mathematical equations and applied logic analysis to find the rate-determining step in the sequence.

An upsurge in the use of activated carbons for treatment of wastewater and effluent from industries and the regeneration of the spent-up carbon by steam activation resulted in a considerable

Table 7 Adsorption Capacity of Impregnated Carbons for NO_2 and CNCl

Impregnant	Weight uptake of NO_2 ($\mu g/cm^2$)	Impregnant	Weight uptake of CNCl ($\mu g/cm^2$)
None	10	None	60
$KMnO_4$	30	Cu (5%)	160
Cu (14%)	110	Cu (5%) + $Na_2Cr_2O_7$ + pyridine	320
Cu (14%) + $KMnO_4$	160	Cu (5%) + $Na_2Cr_2O_7$ + TEDA (1%)	860
Cu (14%) + ClO_2	520	Cu (5%) + $Na_2Cr_2O_7$ + TEDA (3%)	1530

Source: Capon et al. (35).

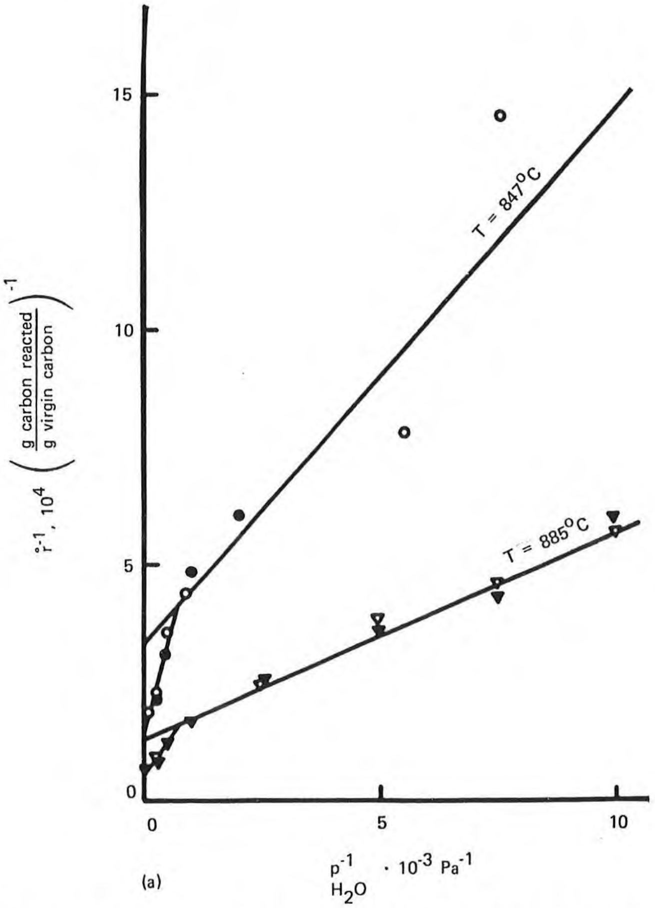

Figure 3 Steam—carbon reaction data for (a) 847 and 885°C (phenol loaded sample, ● ▼; untreated sample, ○ ▽) and (b) 915 and 950°C (phenol-loaded sample, ▲ ■; untreated sample, △ □). [From Krebbs and Smith (41). Reproduced with permission from Pergamon Press.]

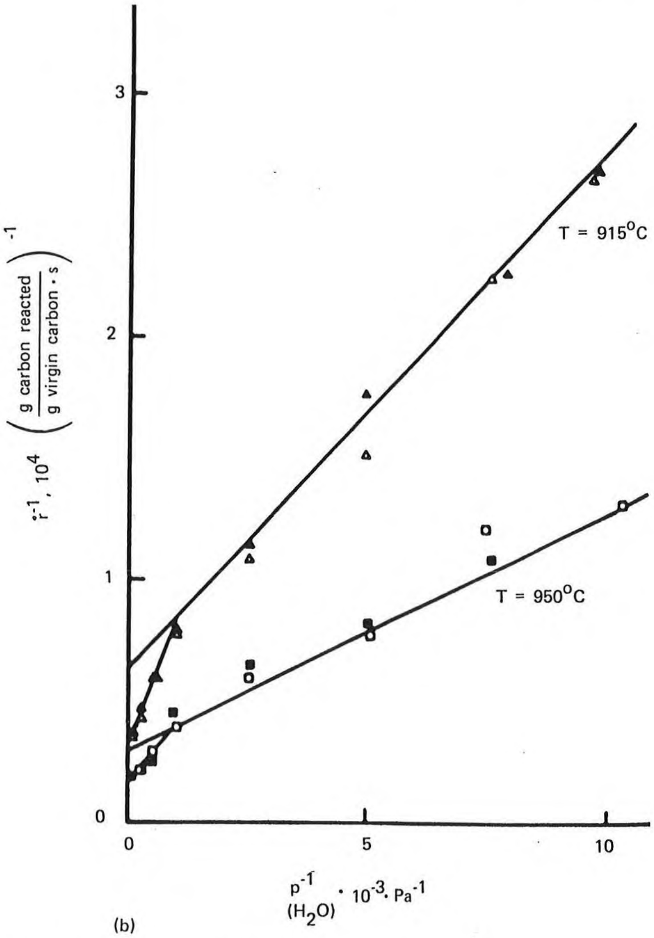

Figure 3 (continued)

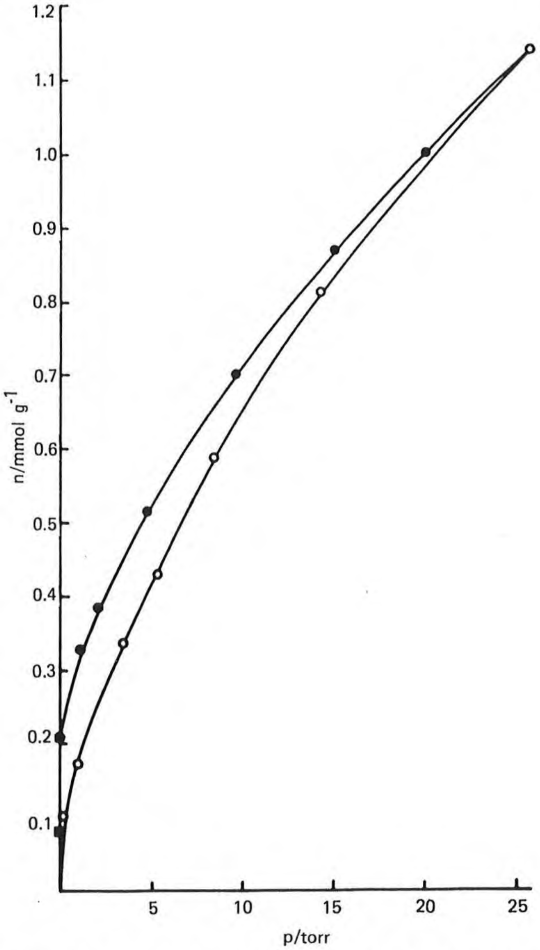

Figure 4 Sorption isotherm at 25°C for PH_3—carbon cloth (sample outgassed at 110°C). Open circle, sorption; closed circle, desorption; close square, desorption at 110°C. [From Hall et al. (42). Reproduced with permission from Pergamon Press.]

amount of research relating to modification of activated carbons by the adsorbate residues left on the surface of these carbons. Umehra et al. (38.39) used sodium dodecyl benzene sulfonate (DBS) as the adsorbate and observed that after thermal regeneration the DBS residue increased the rate of steam–carbon reaction by one order of magnitude, which was attributed to the catalytic effect of metal atoms. Chihara et al. (37) studied activated charcoals having sucrose adsorbed on them, but the residue left after thermal regeneration was so small that it was not possible to conclude if the residue modified the subsequent steam regeneration. Reichenberger (40) adsorbed phenol on an activated carbon and examined the rate of steam regeneration in the temperature range 700–800°C and at steam pressures 10^4–10^5 Pa and observed a 25% increase in carbon gasification. Krebbs and Smith (41) used TGA to study the kinetics of steam activation over a wide range of steam pressures (10_2–10_4 Pa) and temperatures between 850 and 950°C using an activated carbon before and after adsorption of phenol. The rates of steam–carbon reaction were essentially the same for virgin and phenol-loaded carbons (Fig. 3). These workers were of the view that when the residue from thermal decomposition was purely organic, it did not affect the steam gasification rates.

Hall et al. (42) recently carried out detailed and comprehensive investigations into the adsorption of phosphine (PH_3) and water vapor on an activated carbon cloth before and after impregnation with $AgNO_3$ and $Cu(NO_3)_2 \cdot 3H_2O$ from aqueous solutions. The techniques used included adsorption by gravimetric measurements, surface characterization using XPS, SEM (scanning electron microscopy), ED-X-ray analysis (energy dispersive X-ray analysis), and IR spectroscopy to study the corresponding gas phase. The adsorption isotherms in the pressure range 0–25 torr (Fig. 4) indicated that raw cloth had strong affinity for PH_3. Impregnation enhanced the sorption capacity (Fig. 5) of the cloth above a certain pressure limit, which depended on the impregnant content of the carbon cloth, but apparently reduced the adsorption capacity at lower pressures. The isotherms exhibited adsorption–desorption hysteresis with the desorption curve failing to meet the adsorption curve even when the pressure approached zero. However, a second run on the untreated cloth was reversible and did not show hysteresis. The failure of the hysteresis loop to close even after prolonged evacuation indicated that the raw cloth as well as the impregnated samples retained an appreciable amount of PH_3, which was bonded strongly. The amount of PH_3 retained compared to the raw cloth was as much as five times greater when the impregnant was $AgNO_3$ and three times greater when it was $Cu(NO_3)_2 \cdot 3H_2O$. The enhancement in the adsorption of PH_3 was more when the impregnant was $Cu(NO_3)_2$ than when it was $AgNO_3$ with the same molar concentrations of the metal

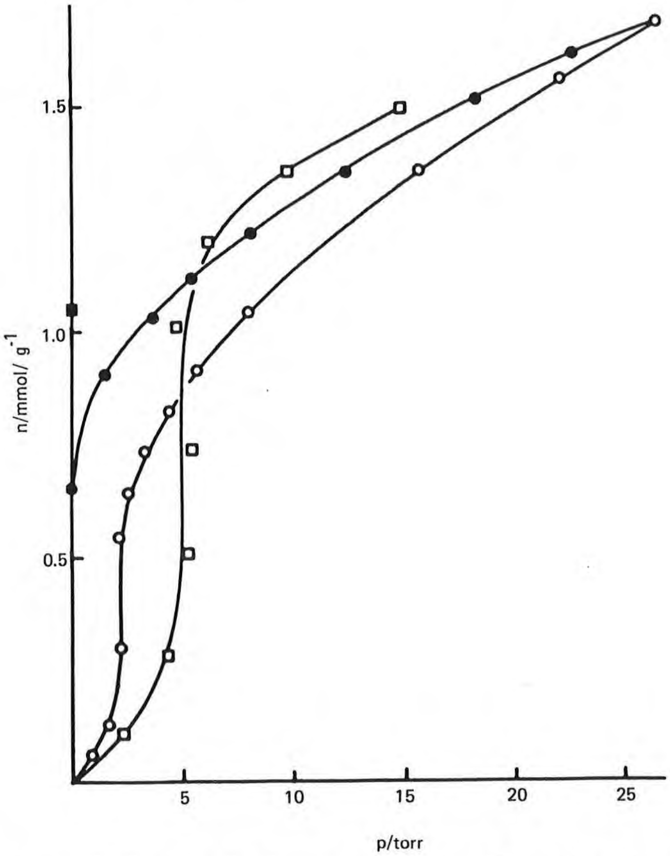

Figure 5 Sorption isotherms at 25°C for PH_3–$CU(NO_3)_2 \cdot 3H_2O$ freshly impregnated carbon cloth (sample outgassed at 25°C) and PH_3–$AgNO_3$ freshly impregnated carbon cloth (>5% Ag, sample outgassed at 25°C). For Cu: open circle sorption; closed circle, desorption. For Ag: open square, sorption; closed square, desorption. [From Hall et al. (42). Reproduced with permission from Pergamon Press.]

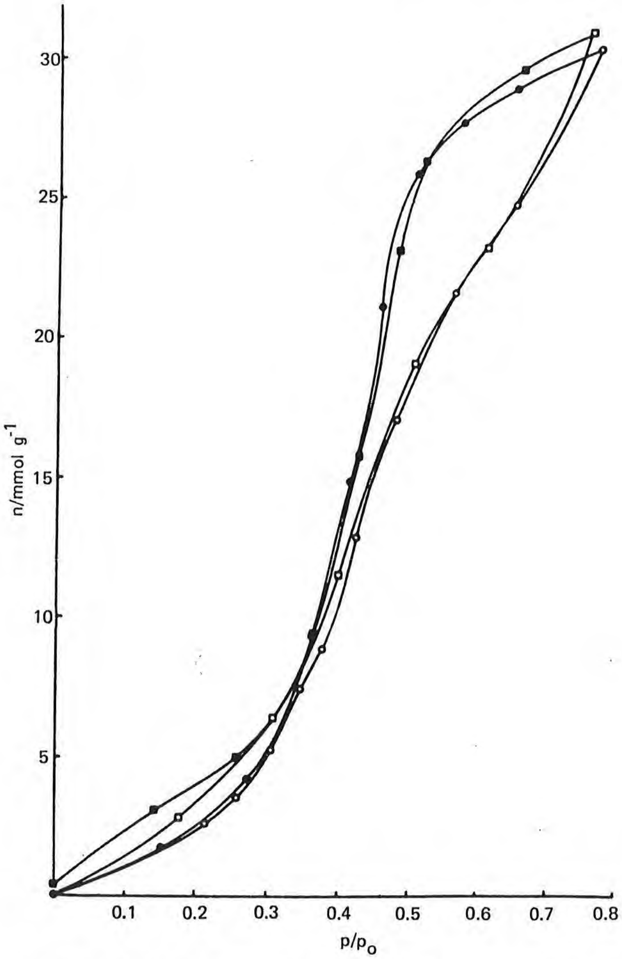

Figure 6 Adsorption isotherms at 25°C for H_2O on raw and on $AgNO_3$-impregnated carbon cloth (= 5% Ag samples outgassed at 25°C). For raw cloth: open circle, adsorption; closed circle, desorption. For Ag impregnated cloth: open square, adsorption; closed square desorption. [From Hall et al. (42). Reproduced with permission from Pergamon Press.]

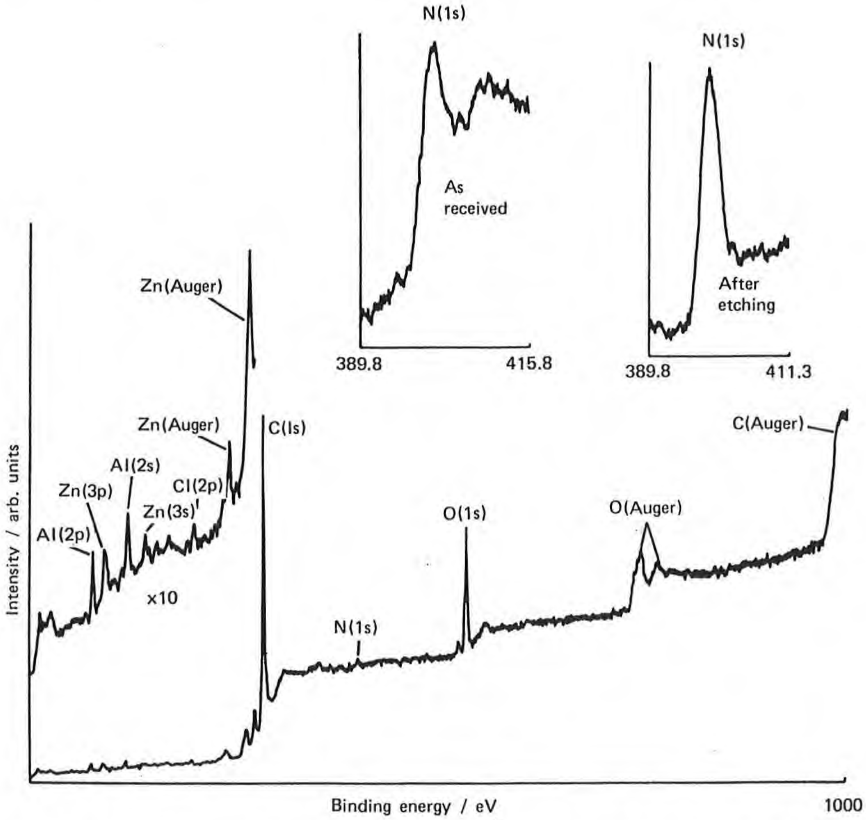

Figure 7 Widescan X-ray photoelectron spectrum of carbon cloth, plus insets of a high-sensitivity scan of the 0–280 eV region with a high resolution scan of the N (1s) signal before and after 25 min etching. [From Hall et al. (42). Reproduced with permission from Pergamon Press.]

ions. Dubinin–Astakhov plots (when $a = 1$) were linear for raw carbon cloth over all pressure ranges but showed deviations from linearity in the low-pressure region for the impregnated carbon cloth. This indicated different mechanisms in adsorption at low- and high-pressure regions.

Water vapor adsorption isotherms at 25°C were type V of the BET classification on raw carbon cloth with a marked hysteresis

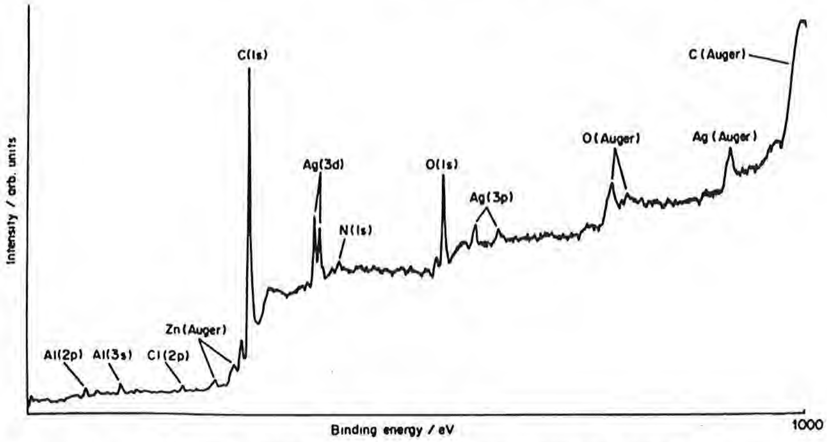

Figure 8 Widescan X-ray photoelectron spectrum of $AgNO_3$-impregnated carbon cloth (= 5% Ag) after 1 min etching. [From Hall et al. (42). Reproduced with permission from Pergamon Press.]

loop. Impregnation with $AgNO_3$ had little effect on the relative pressures studied except below about 0.3 where the uptake was enhanced by as much as 25% during adsorption and even more during desorption. The isotherm also showed a second hysteresis loop (Fig. 6), which failed to close as the pressure approached zero. The nonclosure of the hysteresis loop indicates the amount of water adsorbed irreversibly. The sorption capacity of the $AgNO_3$-impregnated carbon cloth for PH_3 was reduced markedly by the presence of water when exposed to a mixture of PH_3 and water vapors.

Infrared studies of the gaseous species showed the presence of N_2O when the $AgNO_3$-impregnated carbon cloth was exposed to PH_3, although no such IR-active species were observed when raw carbon cloth was exposed to PH_3. The presence of water reduced the amount of N_2O produced in the case of the impregnated cloth. Such species were also observed when bulk $AgNO_3$ or $Cu(NO_3)_2 \cdot 3H_2O$ was reacted with PH_3. This indicates that PH_3 reacts chemically with the impregnant on the carbon cloth surface. SEM and ED-X-ray analysis showed nodular growth of virtually pure silver together with $AgNO_3$ on the surface of the $AgNO_3$-impregnated carbon cloth. After exposure to PH_3, phosphorus was largely confined to areas away from these nodules. XPS spectra (Figs. 7 and 8) showed a layer of $AgNO_3$ together with some metallic silver on the $AgNO_3$-impregnated

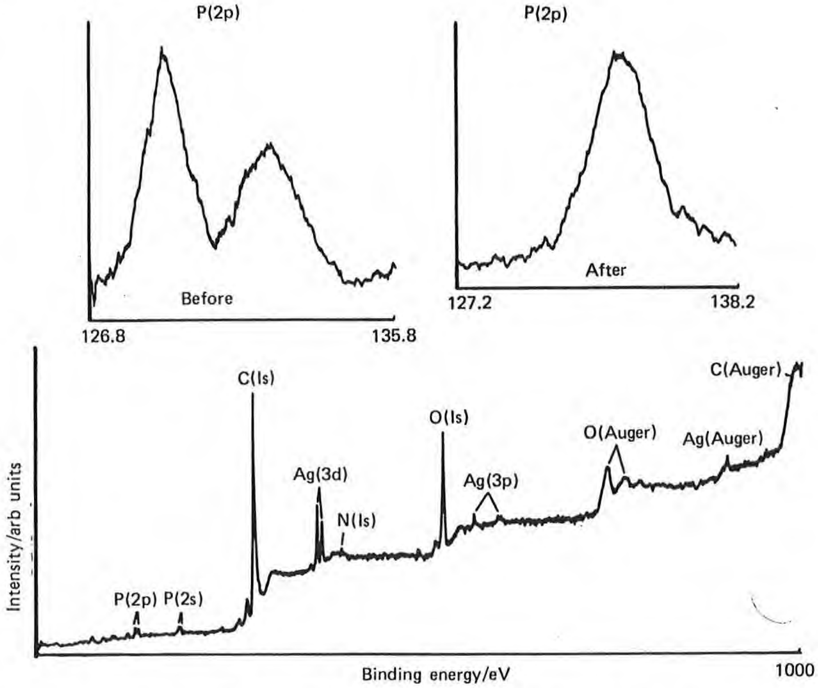

Figure 9 Widescan X-ray photoelectron spectrum of $AgNO_3$-impregnated carbon cloth ($\simeq$ 5% Ag) after exposure to PH_3, plus insets of the P(2*p*) signal before and after 5 days of air exposure. [From Hall et al. (42). Reproduced with permission from Pergamon Press.]

cloth. After exposure to PH_3 the formation of at least two phosphorous compounds, one of which was air sensitive, was indicated (Fig. 9).

Kaistha and Bansal (42a) impregnated an activated carbon with sodium ions by treating the oxidized carbon with appropriate quantities of 0.1 *M* solutions of $NaHCO_3$. The treatments resulted in the impregnation of appreciable amounts of sodium ions, the amount being larger in the case of NaOH treatment. The adsorption isotherms of aqueous oxalic acid on the oxidized and the ion-impregnated carbon (42a) showed a considerable increase in the case of the impregnated carbons, the extent of increase depending on the increase in the degree of impregnation. For example, the amount of oxalic acid adsorbed increased from 0.75 mmol/g for the oxidized carbon to 1.52 and 1.80 mmol/g after impregnation. Furthermore, the amount of oxalic acid adsorbed on the impregnated carbons was very close to the amount of sodium ions impregnated on the carbon surface, indicating that the adsorption of oxalic acid involved an exchange mechanism. This received further support from the observation that when the sodium ions were removed from the carbon surface by treatment with acid and then washing repeatedly with hot distilled water, the adsorption of oxalic acid superimposed almost completely the adsorption on the nonimpregnated carbon at all concentrations. The impregnated carbons had smaller surface area than the original oxidized carbon. When the amounts of oxalic acid adsorbed were calculated per unit surface area, it was found that the impregnated carbons showed a much more enhanced adsorption of oxalic acid, indicating that impregnated carbons have a better efficiency for the removal of oxalic acid from aqueous solutions.

5.3 MODIFICATION OF CARBONS BY HALOGENATION

The treatment of activated carbons, charcoals, and carbon blacks with halogens has been studied by several investigators with a view to modify their surface character. The adsorption of the halogens is both physical (43,44) and chemical and proceeds through several mechanisms, including addition at the unsaturated sites (45–55), exchange with chemisorbed hydrogen (48–55), and surface oxidation of the carbon (45,46,56), depending on the nature of the carbon surface, the oxygen and hydrogen contents of the carbon, the experimental conditions, and the nature of the halogenating species. The halogen fixed on the surface of carbons in the form of carbon–halogen surface compounds is thermally highly stable and can be eliminated on heat treatment in vacuum up to 1000°C if the carbon has no residual hydrogen. However, a part of the halogen could be exchanged with OH groups on treatment with alkali hydroxides and with NH_2 groups on heat treatment with ammonia gas.

Reyerson and co-workers (44,57,58), Alekseeviskii and Likharev (59), and Emmett (60) treated activated carbons and charcoals with chlorine and bromine in the gaseous states and observed that appreciable amounts of the halogens were fixed irreversibly on the carbon surface. The carbon–chlorine or the carbon–bromine complex was very stable and could not be decomposed on high-temperature treatment in vacuum or by refluxing with alkalis. Alekseeviskii and

Table 8 Amount of Chlorine Fixed by Different Carbons

Carbon	Oxygen content (%)	Hydrogen content (%)	Chlorine fixed (meq/g)
Sugar charcoal			
Original	32.52	3.38	6.70
400°-outgassed	16.86	3.37	5.35
500°-outgassed	12.76	3.07	4.21
700°-outgassed	7.48	2.58	2.87
1000°-outgassed	1.42	1.15	2.70
1200°-outgassed	0	1.02	2.57
Coconut shell charcoal			
Original	15.45	1.24	11.35
700°-outgassed	7.25	1.05	5.63
1000°-outgassed	0.52	0.62	3.50
1200°-outgassed	0	0.35	2.31

Source: Puri et al. (51).

Likharev, however, found that the carbons activated in chlorine were better than many of the commercially available materials and suggested that treatment with chlorine gas could be used as an activating process.

The interaction of halogens with carbon blacks was studied by Ruff (61), Boehm et al. (62), and Rivin and Aron (63). Boehm et al. (62) observed that the chlorine fixed on treatment at 400–500°C was roughly equivalent to the initial hydrogen content of the carbon black and was available for reactions with ammonia at elevated temperatures as well as with potassium hydroxide and sodium cyanide on fusion. Rivin and Aron (63), however, found that the reactivity as well as the stability of the carbon–halogen surface compounds formed on treatment with gaseous halogens or from solutions was in the order Cl > Br > I. Thus while all of the iodine could be dissociated, only 80% of the bromine and 60% of the chlorine could be dissociated in the presence of suitable neucleophiles. Puri and Bansal (52), during their interaction of carbon blacks with chlorine, found that only a part of the chemisorbed chlorine could be recovered on boiling under reflux with sodium hydroxide solution (2.5 *N*) or on heat treatment in vacuum at 1000°C.

Puri and co-workers (51, 64) carried out systematic investigations into the formation and properties of carbon–chlorine surface compounds formed on sugar and coconut charcoals associated with varying amounts of oxygen and hydrogen, in the temperature range 35–600°C and at varying pressures of the chlorine. The interaction resulted in the fixation of appreciable amounts of chlorine, the magnitude depending on the temperature of treatment up to 450°C and the oxygen and hydrogen contents of the charcoals. The maximum amounts of chlorine fixed at 450°C were 24% in sugar and 40% in coconut charcoal, and this amount decreased gradually and appreciably on outgassing the charcoals at gradually increasing temperatures (Table 8). The kinetic measurements showed that the reaction between carbon and chlorine was first order.

Puri and Bansal (46) showed that the fixation of chlorine occurs partly by addition at the unsaturated sites vacated by the combined oxygen (47,48) and partly in exchange (substitution) for hydrogen (Table 9). Since original charcoals which had not been outgassed contained few unsaturated sites, the bulk of the chlorine was fixed by exchange with hydrogen (Table 9), as observed by Boehm et al. (62). However, when these charcoals were outgassed, the hydrogen content decreased and unsaturated sites were created by the evolution of oxygen; the chlorine fixed now was more by addition than by substitution. In the case of the chlorination of 1000° outgassed charcoals, which—although they retained about 30% of the total hydrogen content of the original charcoals—were not able to fix chlorine by substitution (Table 9), almost the entire amount of chlorine was

Table 9 Fixation of Bromine by Various Samples of Charcoal and Carbon Black before and after Fixation of Chlorine (values in meq/g)

			Unsaturation as determined by Br_2 uptake from aqueous solution			
Sample	(a) H_2 present in sample	(b) Cl_2 fixed at 450	(c) Before chlorination	(d) After chlorination	(e) Cl_2 fixed by addition [(c−d)]	(f) Cl_2 fixed by substitution [(b) − (e)]
Sugar charcoal						
Degassed at 400°	33.78	6.35	3.12	1.68	1.44	4.91
Degassed at 700°	25.80	3.35	3.76	0.63	3.13	0.23
Degassed at 1000°	11.50	3.09	3.88	0.85	3.03	0.06

Degassed at 1200°	10.20	3.07	3.80	0.86	2.94	0.13
Coconut charcoal						
Degassed at 400°	20.10	10.28	2.40	0.65	1.75	8.53
Degassed at 700°	10.10	5.63	3.16	0.93	2.23	3.4
Degassed at 1000°	6.40	3.39	3.14	1.14	2.00	1.39
Degassed at 1200°	6.10	2.31	3.16	1.24	1.92	0.39
Carbon black						
Philblack-A	3.50*	3.57	0.30	0	0.30	3.27
Spheron-9	5.30	3.31	0.43	0	0.43	2.88
Spheron-6	4.90	3.97	0.62	0	0.62	3.35
Spheron-4	3.80	3.14	0.45	0	0.45	2.69
Spheron-C	2.50	2.65	0.70	0	0.70	1.95
ELF-0	3.80	4.40	0.12	0	0.12	4.34
Mogul	3.00	3.15	0	0	0	3.15

Source: Puri and Bansal (46).

fixed by addition at the unsaturated sites. This is due to the fact that this hydrogen, which could not be desorbed on evacuation at 1000°C, was present in charcoals at less active sites (65) dispersed in the body of the carbon surface or held up in the extremely fine microcapillary pores and was not readily available for exchange with chlorine. This view was further supported by the fact that coconut charcoals, which have relatively coarser porous structure than sugar charcoals, could fix more chlorine by substitution. The carbon blacks, which were essentially nonporous, fixed almost all of their chlorine by exchange with hydrogen (Table 9). These views regarding the fixation of chlorine were substantiated by the chlorination of anthracites by Walker et al. (66) and by Puri and co-workers by their reactions of charcoals with chlorine water (45), a mixture of HCl and H_2O_2 (67), and a mixture of oxygen and chlorine at 400°C (68).

Tobias and Soffer (69) carried out an interesting study of the stepwise chlorination of a carbon cloth (TCM 128), a carbon black (Continex N-110), and a graphitized carbon black (Carbopak B) after outgassing them at 1000°C to eliminate interference of chemisorbed oxygen to chlorine adsorption. The chlorination was found to involve fixation of chlorine and the liberation of hydrochloric acid (Table 10). These workers are of the view that the interaction between chlorine and carbon involved three processes: addition at the olefinic double bonds, exchange with chemisorbed hydrogen, and dehydrogenation of the carbon. The ratio of chlorine fixed to hydrochloric acid formed ($R = Cl_2$ uptake/HCl formed) was taken as a measure of the particular process which dominates in a given step. Thus in the initial stages when the ratio R was higher the most preferred process was the addition of chlorine at the double bond sites followed by exchange with hydrogen and the least favored dehydrogenation. Assuming that when $R > 1$, which was the situation at the first chlorination, the dehydrogenation is negligible and assuming that addition is negligible when $R < 1$, these workers calculated the amounts of chlorine fixed by addition, by exchange, and by dehydrogenation processes (Table 12). The results clearly showed that although clorine addition was the first to occur in both carbon black and active carbon, the exchange reactions were more predominant in the case of carbon blacks (46). The dehydrogenation reactions which occurred to a negligible extent in carbon black were high in active carbon.

To verify that chlorine exchanged with hydrogen these workers (69) carried out a number of chlorination–hydrogenation cycles, measuring the amounts of chlorine fixed and hydrochloric acid formed after each cycle. Significant amounts of hydrochloric acid were produced during both the chlorination and hydrogenation steps together with the fixation of the corresponding gaseous species (Table 12). This indicated that there was an exchange of C–H bond by C-Cl

Table 10 Stepwise Chlorination at 773 K of Carbons after Degassing the Activated Charcoal TCM 128 and the Graphitized Black-Carbolak-8 after Degassing at 1273 K

Step	Cl_2 adsorption (mEq/g)	HCl release (mEq/g)	Ratio of Cl_2 uptake to HCl reformed
Continex N-110			
1	0.225	0.048	4.69
2	0.225	0.203	1.11
3	0.152	0.149	1.03
4	0.140	0.144	0.97
5	0.124	0.122	1.02
6	0.100	0.103	0.97
7[a]	0.135	0.126	1.07
8[a]	0.133	0.143	0.98
9[a]	0.141	0.134	1.05
Total			
TCM 128			
1	0.43	0.32	1.50
2	0.30	0.17	1.76
3	0.18	0.21	0.86
4	0.06	0.05	1.20
5	—	0.02	—
Total	1.02	0.77	1.32
Carbopack-B			
1	0.10	0.01	10
2	0.02	0.02	1
Total	0.12	0.03	4

[a] The cell temperature was cycled once between 773 and 473 K at 1.5 K/min. This enhanced the reaction rate considerably.
Source: Tobias and Soffer (69). Reproduced with permission from Pergamon Press.

bond during chlorination and exchange of C-Cl bond by C-H bond during hydrogenation. Furthermore, after some initial irreversible changes, the system behaved almost reproducibly upon repeated chlorination and hydrogenation cycles. Such reproducibility in fact was attained starting from the second cycle (Table 12), indicating that it was purely an exchange process.

The interaction of carbons with bromine involved the same mechanisms as the interaction with chlorine. Puri and co-workers (47,48) reacted charcoals and carbon blacks with bromine in aqueous solutions. The bromine uptake of the carbons increased with increase in

Table 11 Contributions of Various Reactions Responsible for Cl_2 Interaction with Carbons (data derived from Table 10)

Step	Addition (mEq/g)	Exchange (mEq/g)	Dehydrogenation (mEq/g)
Continex N-110 as received			
1	0.177	0.048	—
2	0.022	0.203	—
3	0.005	0.147	—
4	—	0.136	0.004
5	0.002	0.122	—
6	—	0.100	0.003
7	0.009	0.126	—
8	—	0.173	0.010
9	0.007	0.134	—
Total	0.222	1.153	0.017
TCM 128 as received			
1	0.16	0.32	—
2	0.13	0.17	—
3	—	0.18	0.03
4	0.01	0.05	—
5	—	0.02	0.02
Total	0.30	0.74	0.05
Carbopack-B			
	0.09	0.01	

Source: Tobias and Soffer (69). Reproduced with permission from Pergamon Press.

the temperature of degassing up to 700°C and remained unchanged thereafter. The uptake of bromine was attributed to addition at the ethylenic double bond sites, which were created by the elimination of that part of the associated oxygen that was evolved as carbon dioxide on evacuation (CO_2-complex). Since the entire amount of this complex was desorbed at temperatures below 800°C, the uptake of bromine remained more or less unchanged after this heat treatment temperature. Similar results were obtained by Stearns and Johnson (70) in their reaction of channel blacks with aqueous solutions of bromine.

Bansal et al. (56) reacted polymer carbons with aqueous solutions of bromine and observed that the reaction involved the fixation of bromine as well as the formation of hydrogen bromide (Table 13). The amount of bromine converted into hydrogen bromide was related to surface acidity (Fig. 10) while the amount fixed depended on the

Table 12 Chlorination–hydrogenation Cycles of Activated Carbon Cloth TCM-128, after Degassing at 1273 K (chlorination performed at 778 K; hydrogenation at 1073 K)

Treatment	Chlorine fixed (mEq/g)	Hydrogen fixed (mEq/g)	HCl released (mmol/g)
First cycle			
Chlorination	1.62		1.14
Hydrogenation		2.138	1.26
Second cycle			
Chlorination	2.26		1.92
Hydrogenation		2.14	1.47
Third cycle			
Chlorination	1.94		1.93
Hydrogenation		2.23	1.47
Fourth cycle			
Chlorination	2.13		1.93
Hydrogenation		2.14	1.47

Source: Tobias and Soffer (69). Reproduced with permission from Pergamon Press.

nature of the char and its history of formation. PVDC and Saran chars were prepared from polymers containing no oxygen as a part of their chemical structure, and consequently contained very little associated oxygen with them. These chars therefore had very little unsaturation of the type suggested by Puri et al. (47,48) and Stearns and Johnson (70). On the other hand, these chars were highly microporous; thus a large portion of the bromine was adsorbed in the microcapillary pores. PF (polyfurfuryl alcohol) and UF (urea formaldehyde) chars, which were prepared by the carbonization of oxygen-containing polymers, had unsaturated sites so that bromine could be fixed by addition. These views were supported by the fact that about 30% of adsorbed bromine could be released from brominated PVDC and Saran chars on heat treatment at 50°C (the adsorption was carried out at 30°C), whereas only less than 1% could be recovered from PF and UF chars (Table 14).

Brooks and Spotswood (71), during their reaction of chars obtained from bituminous coal with bromine dissolved in carbon tetrachloride, observed three different types of adsorbed bromine. A part of the adsorbed bromine which could be removed with boiling water or alcohol was attributed to addition compounds of phenanthrene or

Table 13 Hydrogen Bromide Formed and Bromine fixed on Treatment of Polymer Charcoals with Aqueous Solutions of Bromine

Sample	HBr formed (mEq/g)	bromine fixed (mEq/g)	NaOH neutralized (mEq/g)
PVDC-600	18.06	13.02	2.12
Saran-600	13.12	16.10	1.43
Saran-600 (steam activated at 850°C)	3.10	18.24	0.50
PF-140	15.24	21.70	1.83
PF-400	8.42	18.72	0.97
PF-600	2.06	10.04	0.42
PF-900	0.23	5.23	0.16
UF-400	6.07	17.01	0.76
UF-650	4.12	9.22	0.78
UF-850	1.10	5.54	0.07

Key: PVDC = polyvinylidene chloride carbon prepared at 600°C; Saran = saran carbon prepared at 600°C; PF = polyfurfuryl alcohol carbon prepared at temperature indicated; UF = urea formaldehyde resin carbon prepared at temperature indicated.
Source: Bansal et al. (56). Reproduced with permission from Pergamon Press.

anthracene type. The small amount of bromine which was not removed by water but could be recovered by hydrolysis with sodium hydroxide was ascribed to residual aliphatic or alicyclic structures. The rest of the adsorbed bromine, which was difficult to remove except under strongly alkaline conditons, was considered to be substituted for hydrogen in polycyclic ring systems. Watson and Parkinson (72) working with carbon blacks, and Puri et al. (49), working with charcoals and carbon blacks, observed that the interaction with bromine from carbon tetrachloride solutions was partly reversible and partly irreversible (Tables 15,16). The amount of bromide adsorbed reversibly was related to the specific surface area of the carbons (Fig. 11). The irreversibly adsorbed bromine involved both addition at the unsaturated sites and a partial exchange with the chemibound hydrogen. The interaction of charcoals and carbon blacks with bromine vapors (53) was also found to involve addition of bromine at

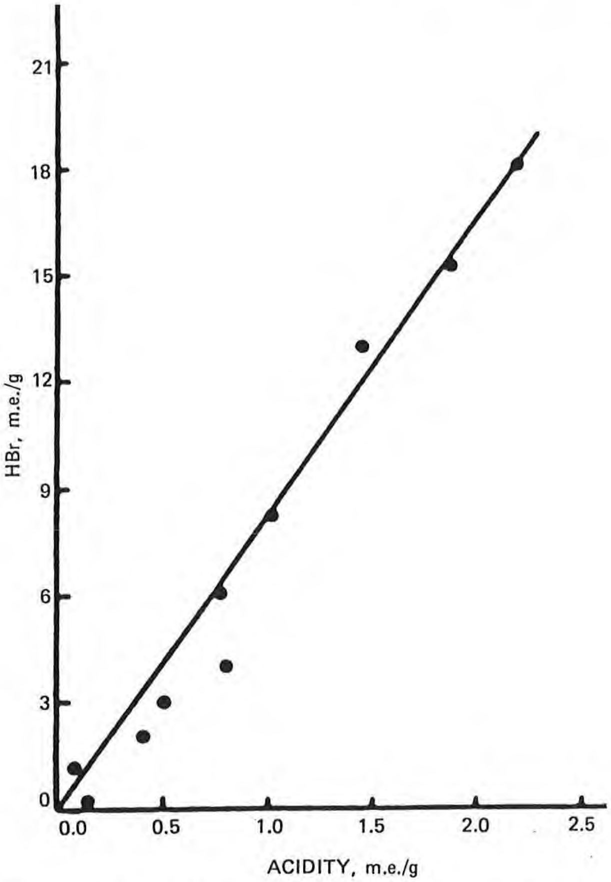

Figure 10 Surface acidity of polymer carbon in relation to hydrobromic acid formed. [From Bansal et al. (56). Reproduced with permission from Pergamon Press.]

the unsaturated sites, exchange with chemibound hydrogen, and dehydrogenation of the carbons in the case of charcoals, but only an exchange reaction in the case of carbon blacks. The amount of bromine fixed was as high as 38% in the original sugar charcoal and about 31% in Spheron-9.

The treatment of active carbons, charcoals, and carbon blacks with iodine solutions in aqueous (73,74) and nonaqueous media does not involve chemisorption of iodine or formation of carbon—iodine surface structures. Consequently, iodine may not be in a position to modify carbon surface properties. It may, however, be mentioned that the adsorption of iodine, being purely physical, has been used

Table 14 Desorption of Bromine on Heat Treatment at Different Temperatures

Sample identification	Bromine fixed (mEq/g)	Bromine desorbed on heat treatment at (mEq/g): 50°C	100°C	150°C	200°C
PVDC-600	18.02	5.41	6.10	7.01	7.52
Saran-600 (steam activated at 850°C)	18.24	5.04	6.91	7.41	8.82
PF-600	10.04	0.22	0.58	0.84	1.10
UF-650	9.22	0.14	0.57	0.72	0.95

Key: PVDC = polyvinylidene chloride carbon; PF = polyfurfuryl alcohol carbon; UF = urea formaldehyde resin carbon.
Source: Bansal et al. (56). Reproduced with permission from Pergamon Press.

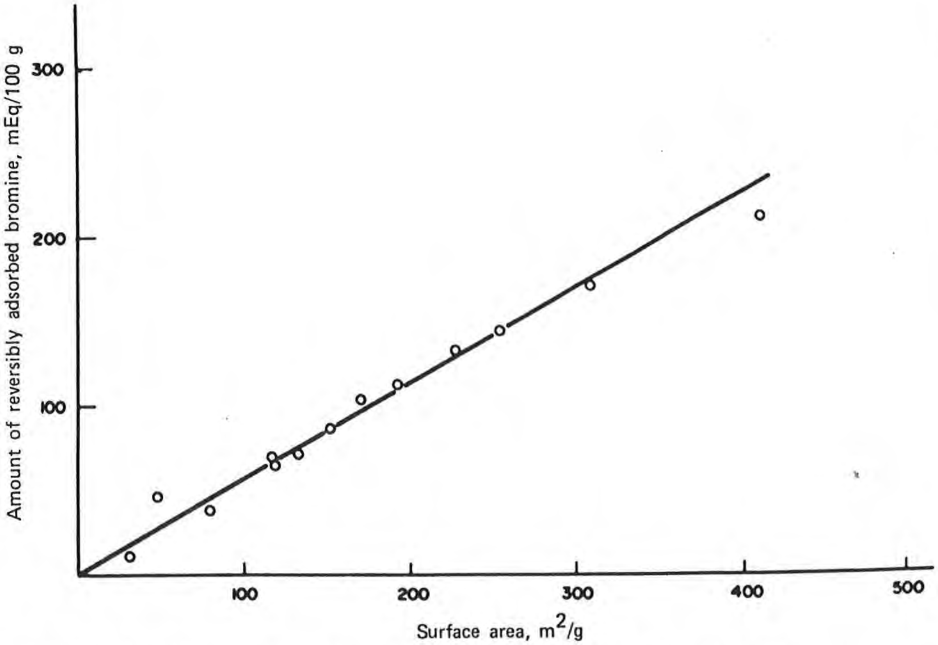

Figure 11 Reversibly adsorbed bromine against surface area. [From Puri et al. (49). Reproduced with permission from Pergamon Press.]

Table 15 Reversible and Irreversible Adsorption of Bromine by Carbon Blacks and Sugar Charcoal of Different Specific Surface Areas, Surface Unsaturations, and Hydrogen Contents

(1) Carbon	(2) Surface area (m^2/g)	(3) Hydrogen content	(4) Bromine adsorbed reversibly	(5) Bromine adsorbed irreversibly	(6) HBr formed (bromine fixed by substitution)	(7) Surface unsaturation (bromine fixed by addition at unsaturated sites)	(8) Bromine unaccounted for [5 - (6 + 7)]
Mogul	308	480	171	132	23	16	93
Mogul-A	228	510	132	131	18	14	99
Elf-0	171	471	105	124	25	13	86
Spheron-C	253	332	144	148	19	70	59
Spheron-4	153	472	86	117	21	41	55
Spheron-9	116	620	65	118	23	42	53
Philblack-A	46	350	26	32	11	11	10
Philblack-I	116	242	68	57	16	21	20
Philblack-E	135	310	72	61	13	22	26
Vulcan-SC	194	140	111	122	11	64	48
Philblack-O	80	310	38	45	12	18	15
Kosmos-40	31	350	11	24	8	9	7
Carbolac	839	470	226	183	32	96	55
Sugar	412	1984	210	393	140	46	207

Source: Puri et al. (49). Reproduced with permission from Pergamon Press.

Table 16 Effect of Outgassing Carbon Blacks and Sugar Charcoal on Reversible and Irreversible Adsorption of Bromine[a]

(1) Carbon	(2) Surface area (m/g)	(3) Bromine adsorbed reversibly	(4) Bromine adsorbed irreversibly	(5) HBr formed (bromine fixed in substitution for hydrogen)	(6) Surface unsaturation (bromine fixed by addition at unsaturated sites)	(7) Bromine unaccounted for [4 - 5 (5 + 6)]
Mogul						
Original	308	171	132	23	16	93
Outgassed at 600°C	335	183	267	13	76	178
Outgassed at 1000°C	328	173	221	0	74	147
Carbolac						
Original	839	226	183	32	96	55
Outgassed at 600°C	815	232	291	20	168	103
Outgassed at 1000°C	760	201	272	11	170	91

Spheron-C						
Original	253	144	148	19	70	59
Outgassed at 600°C	290	173	183	15	88	80
Outgassed at 1000°C	281	160	174	10	82	82
Vulcan-SC						
Original	194	111	122	11	64	47
Outgassed at 600°C	202	118	154	0	80	74
Outgassed at 1000°C	198	104	152	0	76	76
Sugar charcoal						
Original	412	210	393	140	46	207
Outgassed at 600°C	637	282	557	119	380	58
Outgassed at 1000°C	388	201	433	0	375	58

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[a] Columns (2) – (7) expressed in milliequivalents per 100 grams.

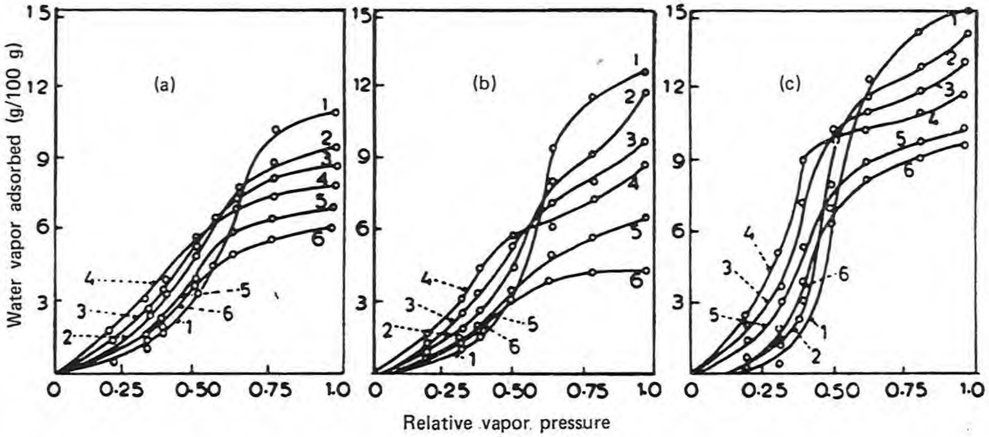
Source: Puri et al. (49). Reproduced with permission from Pergamon Press.

as a measure of surface area by several workers (73–76), although opinions differ as to the way the iodine is adsorbed on carbons. Whereas Hill and Marsh (76) consider adsorption of iodine from aqueous solutions a process of micropore filling and multilayer adsorption, Puri and Bansal (73) view it as a monolayer adsorption from both aqueous and nonaqueous solutions of iodine. These workers obtained surface areas of charcoals and carbon blacks which were comparable to BET (N_2) surface areas. The only important factor in determining surface area by adsorption of iodine is to work under standardized conditions of iodine concentration and the time of contact. According to these workers contacting 1 g of a carbon with 100 ml of 0.15 *M* iodine solution in 2.1 *M* potassium iodide for a period of 72 hr or with 0.3 *N* solution of iodine in benzene or chloroform for 20 days gives reasonable values of surface area. Juhola (74) also observed that adsorption of iodine from aqueous solutions on active carbons was unimolecular while absorption from the vapor phase involved pore filling of micropores (less than 30 Å diameter).

5.3.1 Modification of Surface Properties

The foregoing perusal of the literature on the reactions between carbon and chlorine or bromine shows that carbon–chlorine or carbon–bromine surface structures are formed by addition at the unsaturated sites and/or by exchange of chemibound hydrogen. In addition, these elements may penetrate deep into the microporous structure and require sufficiently high temperature to desorb them. Consequently these chemisorbed or physically adsorbed species may completely modify the surface properties and surface reactions of carbons. For example, the chemisorption of chlorine and/or bromine may produce a polar but nonhydrogen bonding adsorbent similar to the abundant polar carbons that are associated with oxygen surface structures. The carbon–chlorine or carbon–bromine bond may be exchanged with other functional groups to obtain new kinds of surface-modified carbon adsorbents and electrodes. The microporosity and adsorption stereoselectivity of microporous carbons may be modified, giving rise to newer carbons with absolutely new adsorption characteristics and behavior.

Puri and Bansal (77) studied the surface characteristics and surface behavior of sugar and coconut charcoals modified by treatment with chlorine. The true and bulk densities of the charcoals increased linearly with increase in the amount of chlorine chemisorbed by the carbon. The pH of the charcoal, the acid adsorption capacity, and the base neutralization capacities, however, remain unaltered, indicating that the presence of carbon–chlorine surface compounds did not alter the status of surface acidity of the charcoals in any way.



		Chlorine fixed (meq/g)		
Curve	Sample	a	b	c
1	Untreated	0	0	0
2	Chlorinated at 100°	1.09	0.97	0.58
3	Chlorinated at 200°	1.67	1.32	1.70
4	Chlorinated at 300°	2.12	1.69	2.02
5	Chlorinated at 400°	3.50	3.35	3.07
6	Chlorinated at 500°	3.56	3.28	2.99

Figure 12 Water vapor adsorption isotherm on sugar charcoal. [From Puri and Bansal (77).]

The adsorption isotherms of water vapor on sugar charcoals outgassed at 500 (a), 700 (b), and 1000°C (c) containing varying amounts of associated chlorine are presented in Figure 12. These charcoals were essentially free of CO_2-complex so that no secondary effect due to interaction of this complex with water as reported in the literature was possible. The isotherms on the chlorinated samples intersected those on the untreated samples in the 0.5–0.6 relative vapor pressure range in every case, the chlorinated samples taking up more moisture at lower relative vapor pressures and less moisture at higher relative vapor pressures. The effect increased with the fixation of chlorine as long as the temperature of chlorination was 300°C or less. At higher temperatures of chlorination, the sorption values as above decreased (Fig. 12) at all relative vapor pressures in every sample. The increased sorption of water vapors in the lower part of the isotherm cannot be attributed to any chemical or quasi-chemical interaction (such as hydrogen bonding) of water with the chlorinated surface, as is well known for oxygenated carbon surfaces, because in that case the increase would have continued with increase in the chlorine content of the charcoal. These workers (77) are of the view that the fixation of chlorine results more in conditioning the pore structure and size distribution of capillary pores or in changing the location and frequency of active sites involved in the sorption of water vapor than in altering the chemical nature of the surface. This received further support from the shapes of the water isotherms on one of the carbon blacks (Spheron-6) before and after treatment with chlorine (Fig. 13). The isotherm changed shape from type II to type IV and then to type I, indicating a considerable narrowing down of the capillary pores as more and more chlorine was being fixed on the carbon black. The immersional heats of wetting in water of the chlorinated samples also increased only slightly (Table 17), indicating little or no interaction between adsorbed chlorine and water.

The treatment of sugar and coconut charcoals with bromine produced a similar increase in adsorption of water vapor up to a relative vapor pressure of 0.5 and a decrease in adsorption at higher relative vapor pressures. However, in the case of carbon blacks treated with bromine (48), the water vapor adsorption isotherms are shifted bodily upward (Fig. 14) after fixation of bromine, there being almost a uniform increase in all ranges of vapor pressure. The average in adsorption at 0.5 relative vapor pressure in all the four samples was 2.33 mmol/g, while the average fixation of bromine corresponded to 2.58 milliatoms/g, suggesting one molecule of additional water was being adsorbed at each site where a bromine atom had been fixed. The heat of immersion of the brominated samples increased significantly after fixation of bromine, almost in proportion to the amount of bromine fixed (Tables 18, 19).

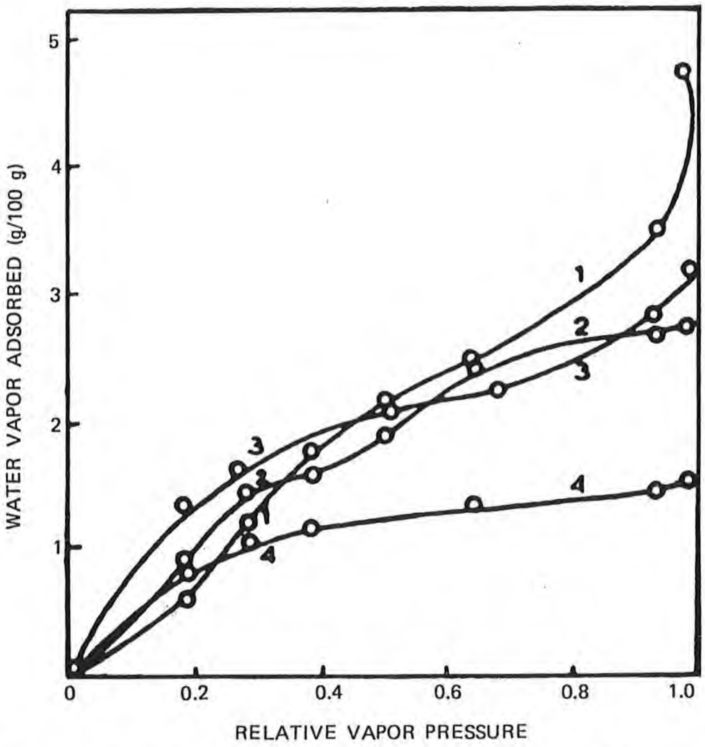


Figure 13 Water vapor adsorption isotherms of Spheron-6 before and after fixation of chlorine. Chlorine fixed: (1) untreated sample, 0; (2) 1–18 mEq/g; (3) 2–45 mEq/g; (4) 3–97 mEq/g. [From Puri and Bansal (77).]

Puri and co-workers (64,77) and Boehm et al. (20) also examined the availability of combined chlorine in carbons for substitution by other functional groups. Exhaustive boiling under reflux with 2.5 *N* sodium hydroxide could hydrolyze only a part of the combined chlorine but the amount hydrolyzed was independent of the amount of chlorine fixed by the carbon. However, the fraction of the chlorine hydrolyzed generally decreased with increase in the temperature of the treatment (Table 20). Almost the same amount of chlorine was eliminated as hydrochloric acid and recovered as ammonium chloride on treatment of the chlorinated samples with dry ammonia gas at 300°C. The amount of nitrogen fixed by the chlorinated sample as a result of ammonia treatment was determined by ultimate analysis and was found to be almost equivalent to the amount of chlorine displaced

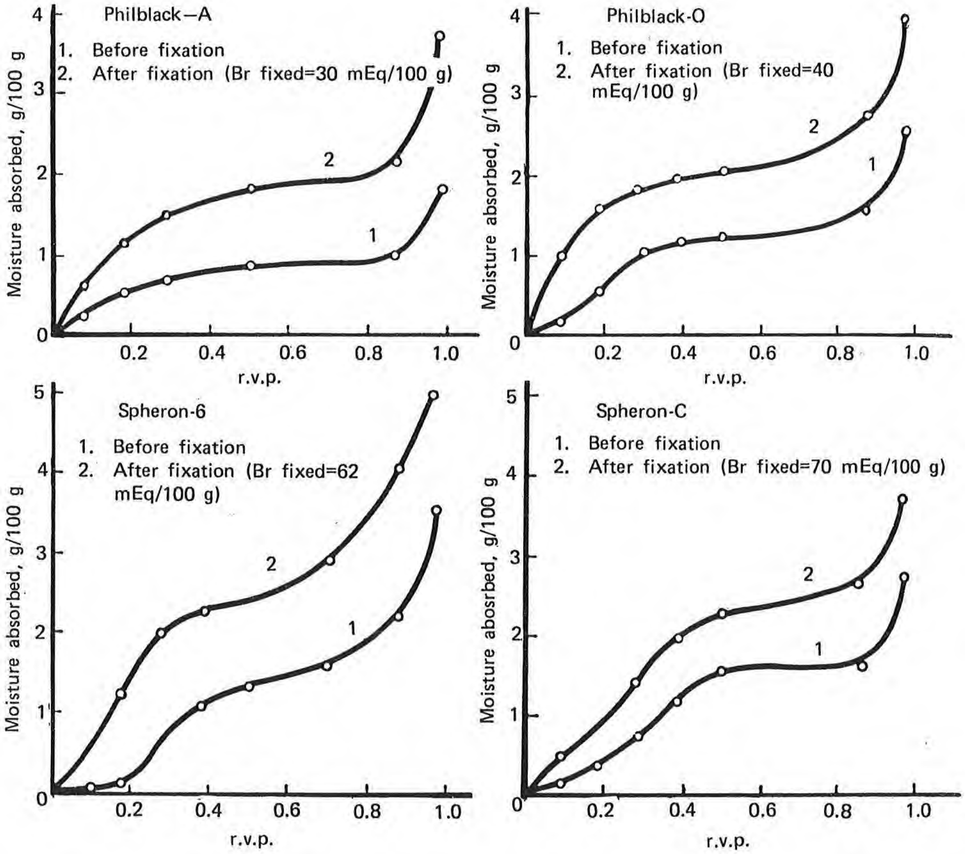


Figure 14 Water adsorption isotherms of carbon blacks before and after fixation of bromine. [From Puri and Bansal (48). Reproduced with permission from Pergamon Press.]

Table 17 Heats of Immersion in Water of Various Samples of Sugar and Coconut Charcoals before and after Fixation of Chlorine

	1000°C-degassed		1200°C-degassed	
Treatment temperature (°C)	Chlorine fixed (mEq/g)	Heat of immersion in water (cal/g)	Chlorine fixed (mEq/g)	Heat of immersion in water (cal/g)
Sugar charcoal				
—	—	5.26	—	4.65
100	1.37	5.51	0.58	4.89
200	1.99	5.97	1.70	5.06
300	2.39	6.51	2.02	5.36
400	3.09	6.45	3.07	5.31
Coconut charcoal				
—	—	3.96	—	2.57
100	1.76	4.26	1.15	2.79
200	2.56	4.65	2.06	3.10
300	3.10	5.15	2.10	3.33
400	3.39	5.21	2.31	3.36

Source: Puri and Bansal (77).

Table 18 Heats of Immersion of Carbon Blacks in Water in Relation to Bromine Fixed

Sample	Bromine fixed (mmol/100g)	Heat of immersion in water (cal/100g)
Philblack-A	0	83
	15	98
Philblack-A	0	195
	20	226
Spheron-6	0	196
	31	226
Spheron-C	0	306
	35	342

Source: Puri and Bansal (48). Reproduced with permission from Pergamon Press.

Table 19 Heats of Immersion of Carbon Blacks in Water Before and After Chlorination

	Heat of immersion (cal/g)	
Sample	Before chlorination	After chlorination
Philblack-A	0.83	1.10
Philblack-E	2.57	2.84
Philblack-I	2.61	2.87
Spheron-9	2.27	2.61
Spheron-6	1.96	2.32
Spheron-4	2.95	3.53
Spheron-C	3.06	3.65
ELF-0	2.90	3.78

Source: Puri and Bansal (48). Reproduced with permission from Pergamon Press.

(Table 21), indicating the replacement of chlorine by amino groups.

The presence of an amino group imparted a basic character to the carbon surface. The pH value of the aqueous suspension was raised from 8.4 to above 9.1 and there was a noticeable increase in the acid adsorption capacity (Table 21). Equivalence between chlorine eliminated, nitrogen fixed and increase in basicity (i.e., increase in adsorption of HCl) on ammonia treatment of the chlorinated carbons clearly indicated that a part of the combined chlorine was available for exchange reactions with other groups. Boehm et al. (62), however, observed that in the case of chlorinated carbon black CK-3, although all of the chlorine could be removed on fusion with potassium hydroxide and about 70% could be removed on treatment with dry ammonia, the increase in the oxygen content in the first treatment and in the nitrogen content in the second treatment was far lower then would be expected for exchange by -OH or $-NH_2$ groups respectively. Reaction of the chlorinated black with sodium cyanide or copper cyanide increased nitrogen content corresponding to decrease in chlorine content, but the hydrolysis of the cyanide groups did not yield carboxyl groups.

Table 20 Chlorine Fixed by Charcoal and Recovered as Chloride Ion on Refluxing with Sodium Hydroxide[a]

Chlorination temperature (°C)	Original		Degassed at 700°		Degassed at 1000°		Degassed at 1200°	
	A	B	A	B	A	B	A	B
Sugar charcoal								
100	1.81	1.15	0.97	0.65	1.37	0.40	0.58	0.35
200	3.80	1.20	1.32	0.65	1.99	0.40	1.70	0.40
300	6.08	1.25	1.69	0.70	2.34	0.45	2.02	0.45
400	6.70	1.20	2.87	0.75	2.87	0.40	2.57	0.45
500	4.00	1.00	3.50	0.70	2.70	0.40	2.56	0.45
Coconut shell charcoal								
100	3.00	1.10	2.69	0.35	1.76	0.56	1.15	0.30
200	4.61	1.25	3.49	0.35	2.56	0.60	2.06	0.35
300	11.38	1.75	4.87	0.40	3.10	0.64	2.10	0.40
400	11.35	1.80	5.63	0.40	3.39	0.64	2.14	0.40

[a] Values refer to the amount of chlorine in milliequivalents per gram. A, fixed; B, hydrolyzed.
Source: Puri et al. (64).

Table 21 Interaction of Sugar and Coconut Charcoals with Ammonia at 300°C

Sample	Chlorine fixed (mEq/g)	Chlorine eliminated as NH_4Cl on treatment with NH_3 (mEq/g)	Nitrogen fixed on treatment with NH_3 (mEq/g)	Increase in the amount of acid adsorbed after treating chlorinated product with NH_3 (mEq/g)	Chlorine hydrolyzed on refluxing with 2.5 *N* NaOH (mEq/g)
1000°C-degassed sugar charcoal treated with chlorine at 400°C	3.09	0.65	0.68	0.71	0.40
1200°C-degassed sugar charcoal treated with chlorine at 400°C	3.07	0.49	0.52	0.53	0.45
1000°C-degassed coconut charcoal treated with chlorine at 400°C	3.39	0.64	0.62	0.59	0.64
1200°C-degassed coconut charcoal treated with chlorine at 400°C	2.31	0.38	0.36	0.40	0.40

Source: Puri and Bansal (77).

Brooks and Spotswood (71), while reacting their brominated chars with copper cyanide in pyridine at 200°C, observed that the combined bromine was almost completely replaced by nitrogen but the cyano groups failed to undergo hydrolysis and were unaffected by treatment with 80% sulfuric acid. Reactions of brominated chars with *n*-butyl lithium in tetrahydrofuran followed by carbonization eliminated bromine completely and increased the oxygen and hydrogen contents of the chars, but the number of carboxyl groups introduced was very small.

Tobias and Soffer (78) recently observed that chlorination of carbons followed by degassing at the same temperature as the chlorination or at higher temperatures creates double bonds which are different from the graphitic surface π bonds in their chemical reactivity. These double bonds, which were in addition to those already existing on untreated carbons, were available for adsorption of hydrogen and hydrochloric acid. These adsorbed species could be partially degassed by thermal cycling, indicating that at least part of these olefinic double bonds were thermally labile and might be available for exchange with other species. Thus carbons modified by chlorine treatment may be of importance in catalysis.

5.4 MODIFICATION OF CARBONS BY SULFUR SURFACE COMPOUNDS

The carbon—sulfur surface compounds have been reported on a wide variety of chars, activated carbons, carbon blacks, and coals. They are formed either during or subsequent to the formation of the carbon. However, their formation, their high thermal stability, the manner and the form in which they can be decomposed, the nature of the carbon surface structure, and their influence on the surface behavior of carbons are some of the factors which have intrigued the surface carbon chemist. These sulfur compounds are nonstoichiometric, falling within a wide range of composition depending on the nature of the carbon, the experimental conditions of its formation, and the magnitude of the surface of the carbon. They frequently contain appreciable amounts of sulfur, which may be as high as 40—50%, even when the contribution of the sulfur contents of inorganic impurities is excluded. These surface compounds can be neither extracted with solvents nor decomposed completely on heat treatment in vacuum at 1000°C but they can be removed completely as hydrogen sulfide on heat treatment in hydrogen between 500 and 700°C.

They are generally formed by heating a carbon in the presence of sulfur vapors (79—88,90,91,102,104,105), or sulfurous gases such as hydrogen sulfide (90,92—96), sulfur dioxide (97—100,104, 105), and carbon disulfide (89,103—105), or during carbonization of organic compounds containing sulfur (83,109), or during carbonization of organic materials in the presence of elementary sulfur (80), or materials yielding sulfurous pyrolytic products (110). The solid sulfur surface compounds so formed by different processes show many similarities with regard to their nonstoichiometric character and chemical behavior, although their formation by the different methods offers different possibilities of sulfur addition to, or substitution in, the carbon lattice.

5.4.1 Formation of Sulfur Surface Structures

Wibaut (79–83) studied the interaction of several charcoals and carbon blacks with sulfur between 100 and 1000°C and observed the chemisorption of appreciable amounts, varying between 18 and 25%, of sulfur with the evolution of small amounts of hydrogen sulfide and carbon sulfide. The sulfur surface compound was very stable and could not be decomposed completely even on heat treatment in vacuum at 1100°C. Juja and Blanke (84), on the other hand, working in the same temperature range, speculated that the fixation of sulfur was partly due to the capillary condensation and physical adsorption and partly due to chemisorption, depending on the nature of the carbon and the experimental conditions. Heat treatment of charcoals with sulfur in a rotating tube furnace at 400°C incorporated about 41% of sulfur in the charcoal, only 12% of which could be washed with solvents (85). The fixation of sulfur lowered the hydrogen content of the charcoal, decreased porosity, and considerably lowered the adsorption of water vapor below 0.5 relative vapor pressure.

Boehm et al. (86,87) could fix about 20% sulfur by heating activated sugar charcoal with sulfur at 600°C in an evacuated tube. The amount of sulfur fixed was equivalent to the amount of oxygen fixed when the same charcoal was oxidized in oxygen at 400°C, indicating that oxygen and sulfur were bonded similarly on the carbon surface. The sulfurized charcoal catalyzed the reaction of sodium azide with iodine which is characteristic of sulfure in sulfide form. Sykes and White reacted coconut charcoal with sulfur (88) and also with carbon disulfide (89), at low pressure, in the temperature range 627–927 K. The treatment of the carbon with sulfur evolved carbon disulfide while the same sample when treated with carbon disulfide developed a pressure of sulfur vapors. This showed that sulfur and carbon disulfide were being adsorbed at the same set of sites, giving rise to different sulfur-containing interconvertible surface structures. The interaction of the carbon with hydrogen sulfide, (89) by a flow method in the same temperature range, fixed appreciable amounts of sulfur, evolving significant amounts of carbon disulfide. However, it could not be ascertained if the carbon disulfide

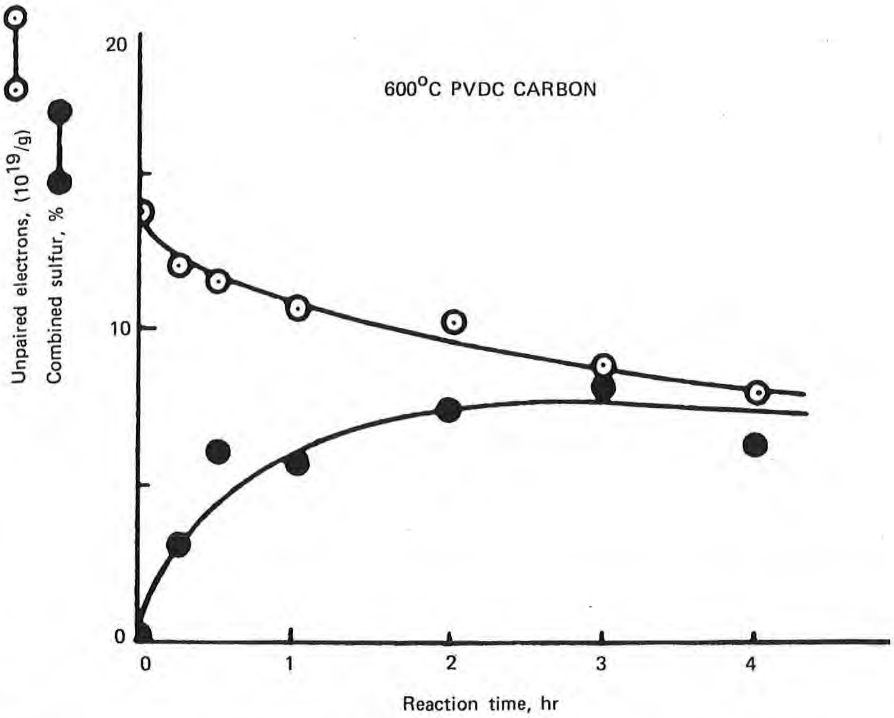


Figure 15 Comparison of sulfur retention and changes in unpaired electron concentration. (Sulfure vapor pressure, 15 mm; reaction temperature, 300°C.) [From Blayden and Patrick (91). Reproduced with permission from Pergamon Press.]

was produced by direct interaction between hydrogen sulfide and carbon or through the formation of some intermediate surface structures.

The interaction of sulfur and hydrogen sulfide with carbon blacks (90) in the temperature range 150–600°C involved two reactions: a rapid reaction, which was directly proportional to the amount of oxygen present as 1,4-quinone groups indicating addition of one sulfur atom for each quinone-type oxygen atom, and a slow reaction which was retarded by the presence of oxygen atoms. The amount of sulfur fixed in the slow reaction was related to the hydrogen content of the carbon, indicating an exchange for hydrogen.

Blayden and Patrick (91) studied the interaction of PVC, PVDC, and cellulose chars, prepared by carbonization at different temperatures between 300 and 500°C, with sulfur vapors at pressures

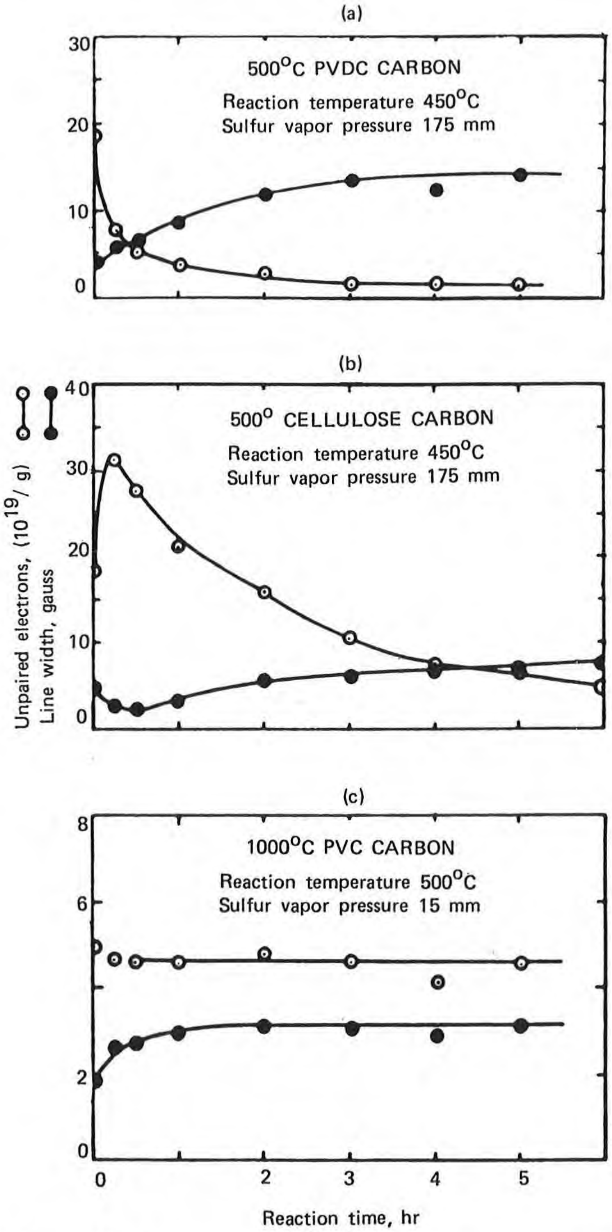


Figure 16 Reaction of representative carbons with sulfur vapor (typical changes of ESR with reaction time). [From Blayden and Patrick (91). Reproduced with permission from Pergamon Press.]

between 15 to 175 mm and with hydrogen sulfide gas. The amount of sulfur fixed depended on the nature of the carbon, the temperature of carbonization of the polymer, the reaction conditions, and the sulfurizing agent and the hydrogen content of the carbon. The reaction with sulfur vapors caused dehydrogenation of the carbon, forming hydrogen sulfide and the fixation of as much as 45% sulfur. The amount of sulfur retained by the carbon decreased with increase in the temperature of treatment. The interaction with hydrogen sulfide appeared to be more complex and less systematic and the sulfur content of the residual product was not more than 4–5%. The sulfur surface structures were stable to nitrous acid and hydrogen peroxide and the combined sulfur could not be extracted by solvents or by sodium hydroxide solution. ESR studies indicated a decrease in the spin concentration progressively with increasing sulfur content in low-temperature carbons sulfurized with sulfur vapors (Fig. 15). There was little or no change in spin concentration in the case of PVC char carbonized at 1000°C (Fig. 16). It was suggested that the sulfur was fixed by chemisorption including spin pairing of sulfur with spin centers and by exchange with combined hydrogen. No definite conclusions were drawn regarding the structure of the resulting surface compound, but it was suggested that surface thioethers and disulfides were the possible surface groups which formed peripheral heterocyclic structures on the layer lattice in the carbon surface or sulfur bridges between the adjacent layers. The presence of sulfide groups was based on the reaction of sodium azide with iodine and on certain reduction reactions.

The interaction of charcoals and carbon blacks with aqueous solutions of hydrogen sulfide (92–96) resulted in the fixation of about 6–7% of sulfur. The fixation of sulfur on oxygen-free carbons occurred by addition at the unsaturated sites (Table 22), whereas the fixation on the oxygenated carbons took place partly by addition at the unsaturated sites and partly by substitution in place of that part of associated oxygen which was evolved as carbon monoxide on evacuation (Table 22). The interaction of carbons with sulfur dioxide has also been studied by several workers (97–100). The reaction with an active carbon (100), between 50 and 650°C in the absence of oxygen in a flow system containing 0.5 vol % SO_2, showed that the chemisorption of sulfur was very small in the temperature range 50–300°C. However, sulfur dioxide reacted with the carbon at 600°C rapidly producing carbon dioxide, carbon monoxide, and elemental sulfur, which was partly deposited in the cooler portion of the reactor and partly fixed by the carbon. Young and Steinberg (101), however, observed that appreciable amounts of sulfur dioxide were chemisorbed by a coconut charcoal on heat treatment with the gas between 400 and 500°C. The IR spectroscopy of the treated charcoal

Table 22 Amount of Sulfur Fixed in Relation to the Degree of Unsaturation in Carbon Blacks Evacuated at 1200°C

Carbon black	Amount of sulfur fixed (mmol/100 g)	Degree of unsaturation as determined by bromine adsorption (mmol/100 g)
Pelletex	6.1	7.0
Kosmos-40	10.2	9.1
Statex-B	6.6	4.9
Philblack-A	18.8	18.0
Philblack-O	22.4	24.0
Philblack-I	10.2	9.1
Spheron-9	30.6	29.1
Spheron-C	40.8	42.3
ELF-O	15.9	17.0
Mogul	33.2	31.3
Mogul-A	30.8	36.9

Source: Bansal and Gupta (96).

showed the formation of sulfate ion by bonding of sulfur dioxide to the surface oxygen.

Puri and co-workers (102–105) carried out a systematic study of the formation, stability, and mechanism of fixation of sulfur by sugar and coconut charcoals associated with varying amounts of oxygen and hydrogen using sulfur vapors, H_2S, CS_2, and SO_2 as sulfurizing reagents at 600°C. Each carbon fixed an appreciable amount of sulfur depending on the amount of associated oxygen and hydrogen of the carbon and the nature of the sulfurizing reagent (Table 25). The sulfur was fixed partly by addition at the unsaturated sites and partly by exchange with certain oxygen structures, which come off as carbon monoxide on high temperature evacuation (Fig. 17). As carbon monoxide was evolved by the decomposition of phenolic and quinonic structures, it was suggested that the exchange with these groups leads to the formation of sulfide and hydrosulfide groups.

The initial hydrogen content of the charcoals also played a significant role in determining the amount of sulfur fixed by a charcoal. It was suggested that nascent hydrogen, which was evolved

Table 23 Amount of Sulfur fixed in Relation to the Degree of Unsaturation in Carbon Blacks

Carbon black	Amount of sulfur fixed (mmol/100g)	Degree of unsaturation as determined by bromine adsorption (mmol/100g)
Furnace blacks		
Pelletex	15.0	2.5
Kosmos-40	20.5	4.6
Statex-B	21.5	11.0
Philblack-A	25.5	15.0
Philblack-O	36.2	21.2
Philblack-I	47.5	25.4
Vulcan-SC	56.0	29.2
Channel blacks		
Spheron-9	71.3	17.2
Spheron-C	83.5	27.2
ELF-O	71.0	2.0
Mogul	130.5	0
Mogul-A	133.5	0
Oxidized blacks		
Spheron-9	65.2	13.2
Philblack-I	45.1	19.8

Source: Bansal and Gupta (96).

from the carbon during the treatment at 600°C, reacted with the sulfurizing agent to produce monoatomic sulfur as

$$S_2 + 2H \longrightarrow H_2S + S$$

$$CS_2 + 2H \longrightarrow H_2S + C + S$$

$$SO_2 + 4H \longrightarrow 2H_2O + S$$

Since H_2S could not undergo such a reaction with hydrogen, the amount of sulfur fixed on treatment with this reagent was not influenced by the hydrogen content of the charcoals (Fig. 18).

Table 24 Fixation of Sulfur on Various Samples of Sugar and Coconut Charcoal on Treatment with Different Sulfurizing Reagents at 600°C

(1)	(2)	(3)	(4)	(5)	(6)
		Unsaturation as determined by Br_2 uptake			
Sample	Sulfur fixed (mEq/g)	Before fixation of sulfur	After fixation of sulfur	Sulfur fixed by addition (mEq/g) [(3) - (5)]	Sulfur fixed by a substitution process (mEq/g) [(2) - (5)]
		Using sulfur as sulfurizing reagent			
Sugar charcoal					
Original	12.3	3.1	0.5	2.6	9.7
400°-outgassed	11.1	3.5	0.2	3.3	7.8
700°-outgassed	7.3	3.8	0	3.8	3.5
1000°-outgassed	5.2	3.8	0	3.8	1.4
Coconut charcoal					
Original	13.5	3.0	0	3.0	10.5
400°-outgassed	10.5	3.4	0	3.4	7.1
700°-outgassed	8.4	3.6	0	3.6	4.8
1000°-outgassed	4.8	3.6	0	3.6	1.2
		Using hydrogen sulfide as sulfurizing reagent			
Sugar charcoal					
Original					
400°-outgassed	7.0	3.1	0.1	2.9	4.6
700°-outgassed	6.5	3.5	0	3.5	3.5
1000°-outgassed	5.5	3.8	0	3.8	2.7

Coconut charcoal					
Original	7.2	3.0	0	2.9	4.3
400°-outgassed	7.1	3.4	0	3.4	3.7
700°-outgassed	5.9	3.6	0	3.6	2.3
1000°-outgassed	4.3	3.6	0	3.6	0.7
	Using carbon disulfide as sulfurizing reagent				
Sugar charcoal					
Original	12.2	3.1	0	3.1	9.1
400°-outgassed	12.3	3.5	0	3.5	8.8
700°-outgassed	8.1	3.8	0	3.8	4.3
1000°-outgassed	5.0	3.8	0	3.8	1.2
Coconut charcoal					
Original	14.2	3.0	0	3.0	11.2
400°-outgassed	14.2	3.4	0	3.4	10.8
700°-outgassed	11.3	3.6	0	3.6	7.7
1000°-outgassed	5.5	3.6	0	3.6	1.9
	Using sulfur dioxide as sulfurizing reagent				
Sugar charcoal					
Original	17.0	3.1	0.2	2.9	14.1
400°-outgassed	16.6	3.5	0	3.5	13.1
700°-outgassed	10.8	3.8	0	3.8	7.0
1000°-outgassed	5.4	3.8	0.3	3.5	1.9
Coconut charcoal					
Original	14.7	3.0	0	3.0	11.7
400°-outgassed	13.2	3.5	0.3	3.2	10.0
700°-outgassed	9.7	3.6	0	3.6	6.1
1000°-outgassed	4.2	3.6	0.3	3.3	0.9

Source: Puri and Hazra (105). Reproduced with permission from Pergamon Press.

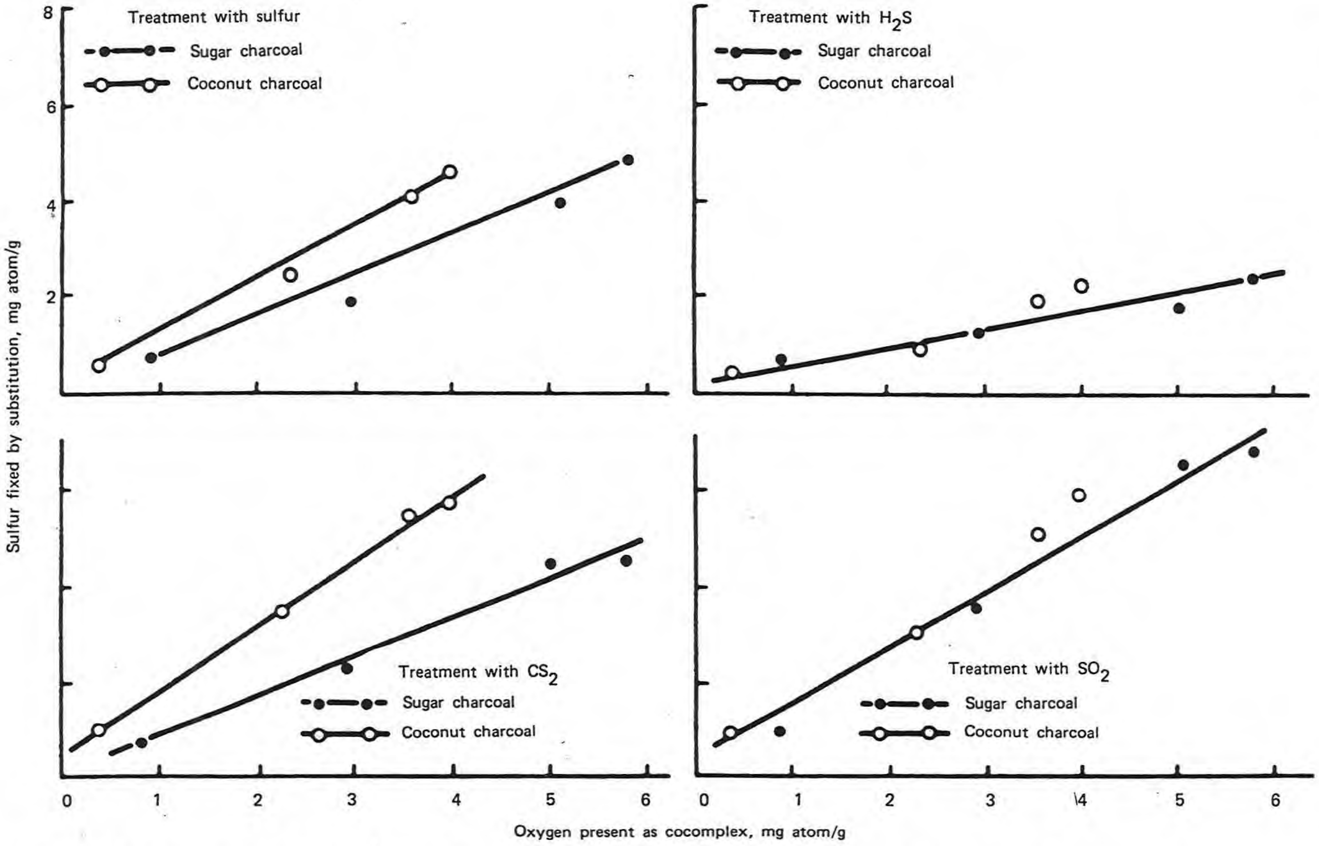


Figure 17 Amount of sulfur fixed by "substitution" in relation to oxygen content present as CO-complex. [From Puri and Hazra (105). Reproduced with permission from Pergamon Press.]

Table 25 Decomposition of Carbon-Sulfur Surface Complex formed on 400°-Outgassed Sugar Charcoal on Heating in a Current of Nitrogen at Different Temperatures

Temperature of heating in nitrogen (°C)	Sulfur evolved as (mEq/g):				Sulfur left in the residue (mEq/g)
	Free sulfur	H_2S	CS_2	SO_2	
	Complex formed on treatment with H_2S (initial sulfur content = 7.50 mEq/g)				
400°	0	0	0.39	0	6.85
500°	0	0.21	0.62	0	6.37
700°	0.10	1.50	0.69	0	4.52
900°	0.12	2.51	1.01	0	3.31
1000°	0.12	3.12	3.04	0	0.23
	Complex formed on treatment with SO_2 (initial sulfur content = 16.6 mEq/g)				
600°	0.12	1.23	0.40	0.95	13.15
800°	0.25	1.41	2.20	1.13	10.20
1000°	0.32	2.10	6.92	1.20	4.62
1200°	0.41	2.70	10.21	1.20	0.83

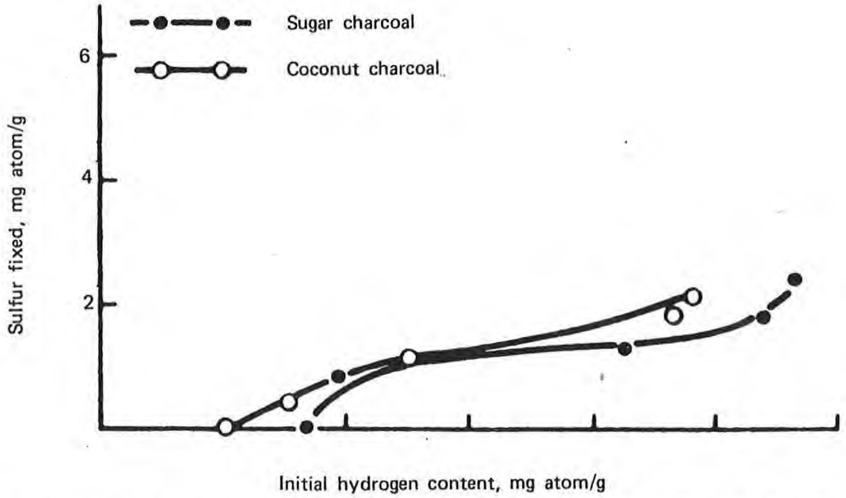


Figure 18 Amount of sulfur fixed by "substitution" in relation to hydrogen content of the various charcoals. [From Puri and Hazra (105). Reproduced with permission from Pergamon Press.]

The carbon–sulfur surface compound was highly stable and could not be recovered on boiling with 2.5 *N* sodium hydroxide solution under reflux for 12 hr (106) and could be recovered only partly on heat treatment in vacuum or in nitrogen at 1000°C (Table 25). However, it could be decomposed completely on heat treatment in hydrogen at 900°C. It was not possible to identify exactly the sulfur-containing surface structures, but Puri et al. (104) explored the probable nature of these groups by estimating the amount of sulfur recovered on treatment of the sulfurated carbons with oxidizing solutions such as aqueous chlorine, acidified potassium chlorate, and concentrated nitric acid. They observed that except in the case of surface compounds formed with sulfur dioxide, only a part of the bonded sulfur could be recovered even with the most drastic treatment with nitric acid at 110°C (Table 26). The amount of sulfur recovered varied up to 10% for the carbon disulfide–treated product and was almost 100% with the sulfur dioxide–treated product. This showed that different types of sulfur structures were formed by different treatments. These workers speculated that the treatment with sulfur dioxide produced readily oxidizable sulfoxides and sulfone structures as well as sulfide and hydrosulfide groups. The formation of sulfoxide and sulfone groups was evidenced by the chemisorption of appreciable amounts of oxygen during the reaction of carbons with sulfur dioxide.

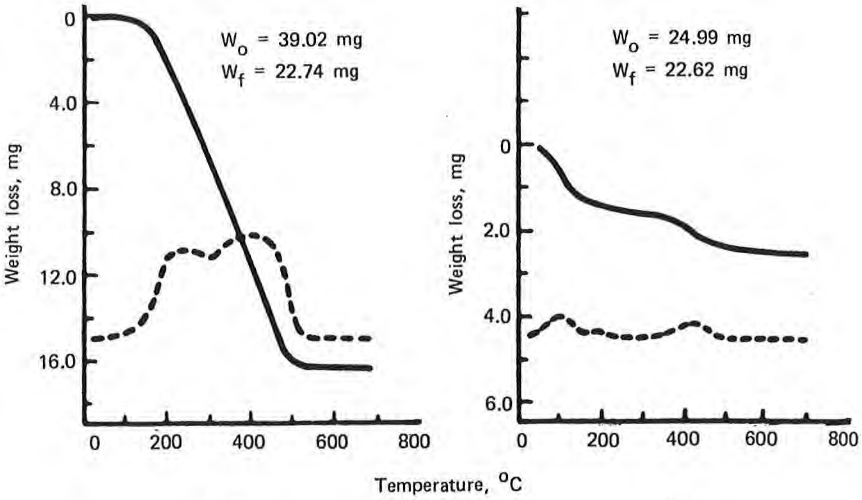
When the surface compounds were formed by treatment with hydrogen sulfide or sulfur vapors, the amount of sulfur recovered by oxidation with nitric acid corresponded, fairly closely, to the amount of sulfur fixed by exchange (Table 24) and the amount not recovered to the amount fixed by addition at the unsaturated sites. The former was attributed to sulfides and hydrosulfides and the latter to highly stable sulfur-containing aromatic ring structures of the carbon layers. The presence of sulfide groups was evidenced by the catalysis of the sodium azide–iodine reaction by the sulfurized carbons. In the case of carbon disulfide–treated carbons, the sulfur recovered was very small (≈ 6–8% of the total fixed). Since some carbon also is deposited in this reaction, it was suggested that some new peripheral heterocyclic structures were condensed on the layer lattices in the carbon surface.

Chang (107) prepared surface sulfur compounds by heating activated carbons, carbon blacks, graphon, petroleum pitches, and polymer chars with carbon disulfide, H_2S, $SOCl_2$ (thionyl chloride), and SO_2, in the temperature range 800–900°C. Sulfur compounds containing greater than 30% sulfur were obtained. However, no detectable amount of sulfur could be fixed on graphon. Thermogravimetric analysis of the surface compounds showed the formation of three different surface structures for activated carbons (Fig. 19). A major portion of the combined sulfur was weakly held and could be recovered with carbon disulfide or on heat treatment at 280°C. The

Table 26 Recovery of Sulfur Fixed on Treatment of Charcoals with Various Sulfurizing Reagents on Treatment with Hot (110°) Nitric Acid

Sample	Total sulfur fixed (mEq/g)	Amount of sulfur recovered as H_2SO_4 (mEq/g)
400°-outgassed sugar charcoal		
Treated with SO_2	16.60	15.06
Treated with H_2S	7.00	3.18
Treated with S	11.10	4.12
Treated with CS_2	12.30	0.76
400°-outgassed coconut charcoal		
Treated with SO_2	13.20	11.90
Treated with H_2S	7.10	3.25
Treated with S	10.50	5.06
Treated with CS_2	14.20	0.82
1000°-outgassed sugar charcoal		
Treated with SO_2	5.40	4.90
Treated with H_2S	5.50	1.55
Treated with S	5.20	1.68
Treated with CS_2	5.00	0.56
1000°-outgassed coconut charcoal		
Treated with SO_2	4.20	3.90
Treated with H_2S	4.30	0.65
Treated with S	4.80	1.40
Treated with CS_2	5.50	0.32

Source: Puri et al. (104).



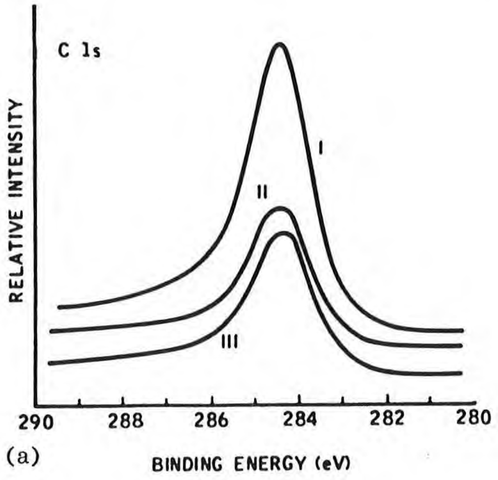
(a) (b)

Figure 19 Thermal gravimetric analyses on the reaction product between Pittsburgh CPG and sulfur (a) before and (b) after CS_2 washing. [From Chang (107). Reproduced with permission from Pergamon Press.]

second type of surface structure was stable to carbon disulfide washing and could be recovered on heat treatment at about 450°C. The third sulfur structure, which these workers called as C_xS, was chemically stable to KOH (9 *N*, 72 hr) and after an initial loss of a small percentage of sulfur was stable even to strong oxidizing agents such as HNO_3 (5 *N*, 72 hr), HCl (5 *N*, 24 hr), and to heat treatment in Ar at 700°C. X-ray diffractometry and electron microscopy of C_xS surface compound showed that it had a disordered structure. ESCA spectra (Fig. 20) showed a carbon 1s binding energy of 284.3 eV and a sulfur $2P_{3/2}$ binding energy of 163.7 eV. Chang postulated that these binding energies and the FTIR absorption bands at 1180 and 1150 cm^{-1} (Fig. 21) suggest that the surface structures on C_xS were thiocarbonyls (> C = S) and thiolactones ($\overset{S}{\underset{C}{\rangle}}c = s$) analogous to carbonyls and lactones existing on the surface of activated carbons. carbons.

5.4.2 Modification of Carbon Surface by Sulfur Surface Compounds

It is apparent that almost all types of carbons can fix appreciable amounts of sulfur-forming sulfur surface compounds. It is also recognized that sulfur is bonded to the peripheral carbon atoms,



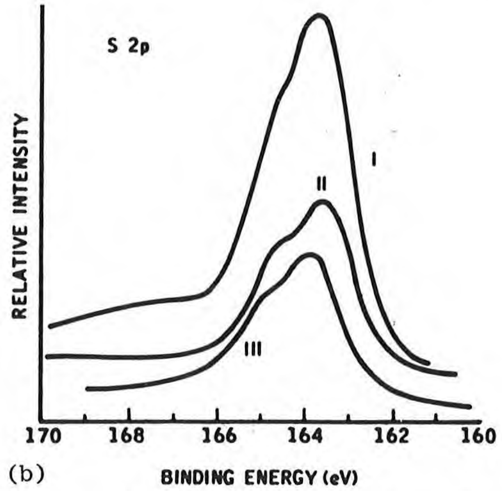


Figure 20 (a) XPS spectra of carbon 1*s*: (I) C_2S (PVDF); (II) mixture of PVDF charcoal and 24% sulfur; (III) C_2S (sucrose). (b) XPS spectra of sulfur 2*p*: (I) C_2S (sucrose); (II) mixture of PVDF charcoal and 24% sulfur; (III) C_2S (PVDF). [From Chang (107). Reproduced with permission from Pergamon Press.]

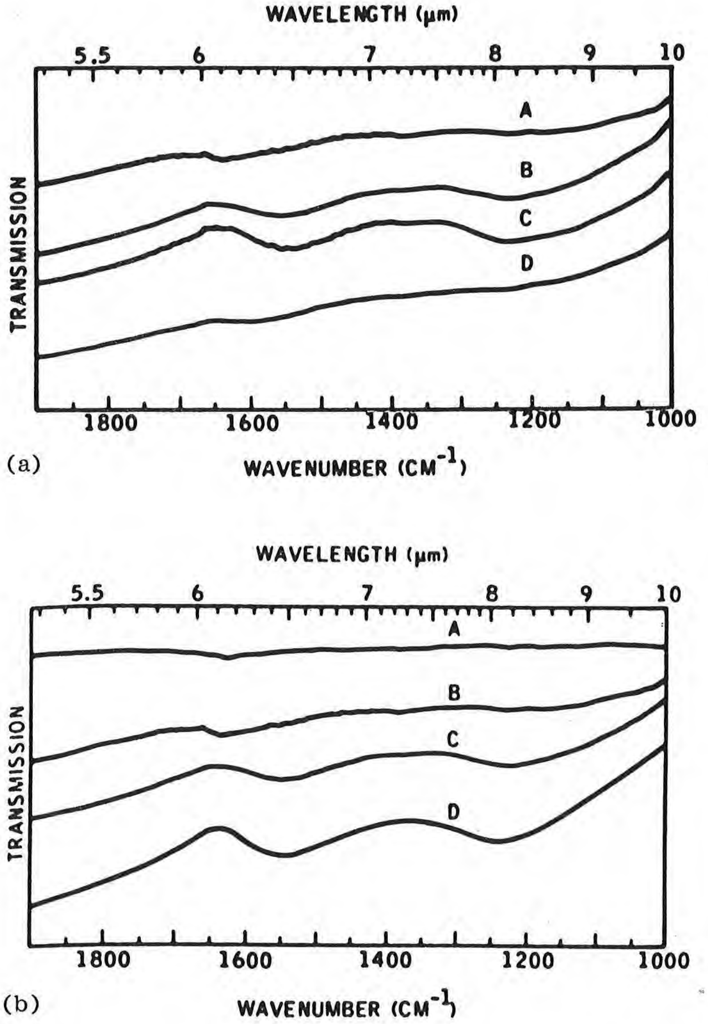


Figure 21 (a) FTIR spectra in the region 1000–1900 cm^{-1}: (A) PVDF charcoal vs. air; (B) C_xS (PVDF) vs. air; (C) C_xS (sucrose) vs. air; (D) (PVDF charcoal + 24.8% sulfur) vs. air; (b) FTIR spectra in the region 1000–1900 cm^{-1}: (A) KBr vs. air; (B) PVDF charcoal vs. air; (C) C_xS (PVDF) vs. air; (D) C_xS (PVDF) vs. PVDF charcoal. [From Chang (107). Reproduced with permission from Pergamon Press.]

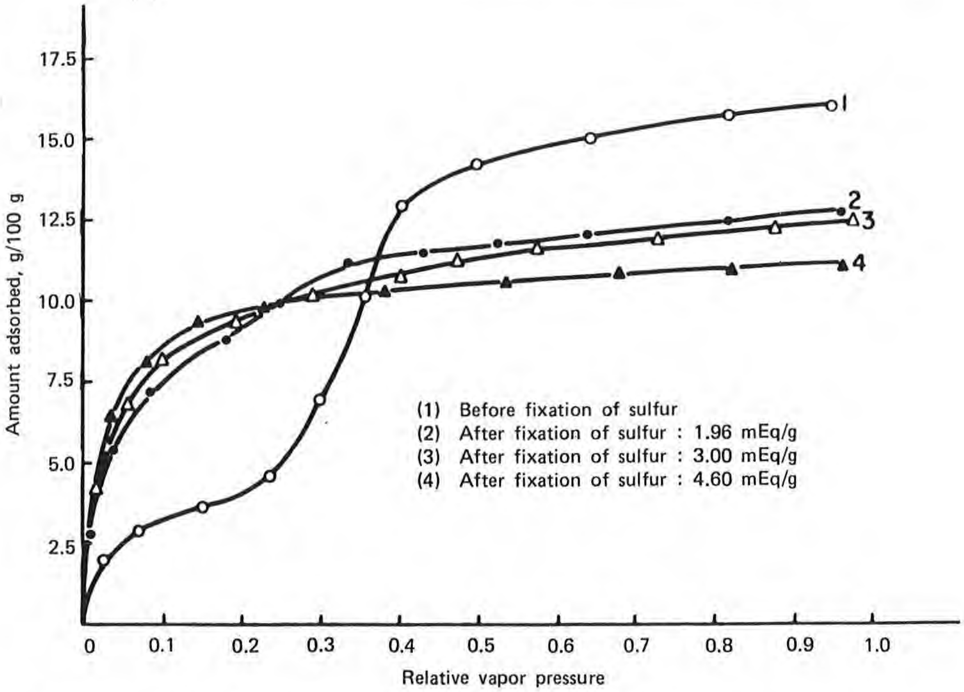


Figure 22 Water vapor adsorption isotherm on 700°C outgassed sugar charcoal before and after fixation of sulfur. [From Puri and Hazra (105). Reproduced with permission from Pergamon Press.]

penetrates into the porous structure, is added at the double bond sites, and is exchanged for hydrogen as well as oxygen associated with the carbon surface. Since the peripheral carbon atoms due to unsatisfied valencies, the unsaturated active sites, and the associated oxygen determine the surface reactions and adsorption characteristics of carbons, it is reasonable to believe that the formation of surface sulfur complexes should modify the behavior of carbons. The formation of carbon—sulfur surface compounds is well known but their influence in modifying carbon surface properties has not been studied systematically.

The influence of sulfur surface compounds on the adsorption behavior of carbons toward polar and nonpolar vapors of varying molecular dimensions was examined by Puri and Hazra (105). The adsorption of water vapors increased appreciably at relative vapor pressures lower than 0.4 and decreased at higher relative pressures (Fig. 22). The effect increased with increase in the amount of sulfur fixed and was attributed to the variation of the pore size distribu-

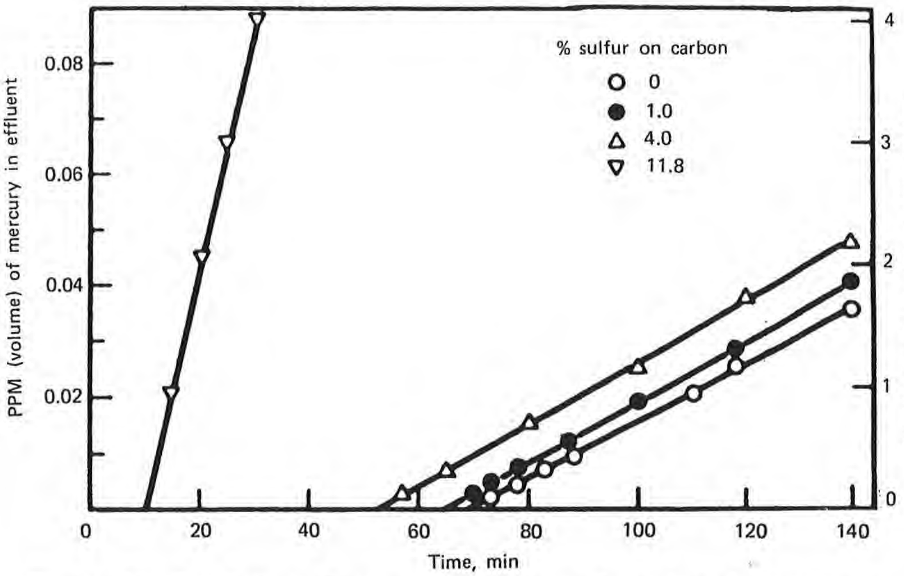


Figure 23 Breakthrough curves of mercury in a dry air stream at 25°C from Saran carbon beds containing varying amounts of sulfur. [From Sinha and Walker (108). Reproduced with permission from Pergamon Press.]

tion caused by the fixation of sulfur along the pore walls. A gradual change in the shape of the isotherm with increasing amounts of sulfur in the carbon indicated that the carbon had become highly microporous. Calculation of the pore size distribution by the Kelvin equation showed a decrease in the pore size from a very wide range to about 10–12 Å. The charcoal, however, could still adsorb appreciable amounts of water vapor. The adsorption isotherms of methanol and benzene vapors, which have higher cross-sectional areas (16.7 $Å^2$ and 41 $Å^2$ respectively) compared to water (cross-sectional area 10.5 $Å^2$), indicated that these larger molecules found smaller and smaller excess as more and more sulfur was being incorporated into the charcoals. There was very little adsorption of benzene and no adsorption of still bigger molecules such as α-pinene. The charcoal behaved as a molecular sieve after the fixation of sulfur. Thus fixation of sulfur could be developed as a method for preparing carbon molecular sieves.

Sulfurized Saran carbon carbonized at 900°C and loaded with varying amounts of sulfur between 1 and 12% was used by Sinha and Walker (108) for the removal of mercury vapors from the air stream using an atomic absorption spectrometer. The contaminated air stream

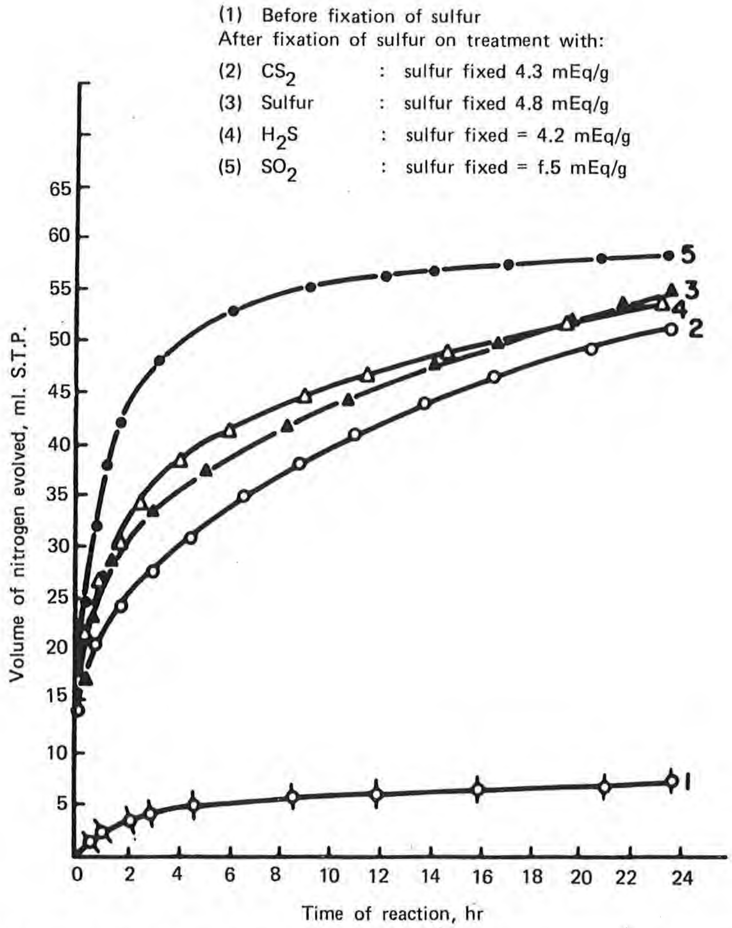


Figure 24 Rate of the sodium azide–iodine reaction in the presence of 700°-outgassed sugar charcoal before and after fixation of sulfur.

was prepared by bubbling air through a mercury bath maintained at 24°C and containing 2.2 ppm by volume of mercury. The breakthrough profile of mercury from beds of charcoal containing different sulfur contents (Fig. 23) showed that increased sulfur content decreased the breakthrough time. Once breakthrough occurred, the rate of mercury buildup in the effluent from carbons containing up to 4% sulfur was independent of the amount of sulfur in the carbon. Introduction of moisture into the contaminated stream to the extent of 1.5% by volume markedly reduced the breakthrough time. However, when the contaminated stream was passed through the carbon

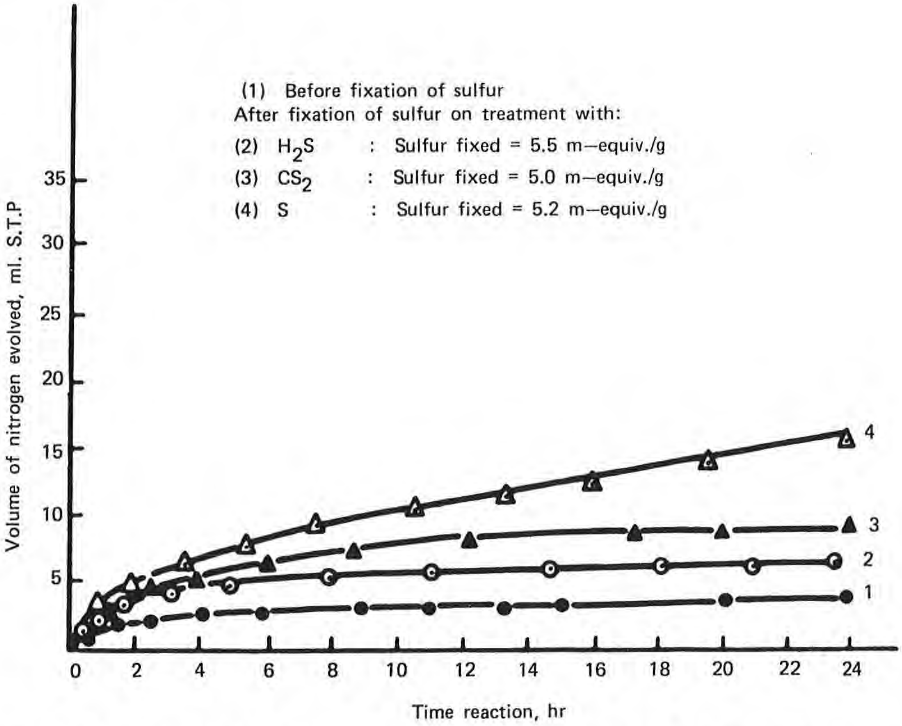


Figure 25 Sulfurized carbons as catalysts for sodium azide-iodine reaction. [From Puri and Hazra (105). Reproduced with permission from Pergamon Press.]

bed at 150°C, the breakthrough time of the sulfurized carbons increased and the mercury buildup in the effluent stream was also very slow compared to the unsulfurized carbon. This greater capacity of the sulfurized charcoal at 150°C for mercury was attributed to its reaction with sulfur on the carbon surface forming mercuric sulfide. However, attempts to recover Hg^{2+} ions from aqueous solutions by sulfurized Saran carbons did not show any promise.

The sulfurized carbons also catalyze the sodium azide–iodine reaction (86,91,105). The results of one such study by Puri and Hazra (105) are shown in Fig. 24. The sulfurized product obtained on reacting 1000°-outgassed sugar charcoal with sulfur, hydrogen sulfide, and carbon disulfide (Fig. 25) was a much less effective catalyst. This was attributed to the fact that in this charcoal the sulfur was present in the form of heterocyclic ring structures and only sulfur present as sulfides can catalyze this reaction.

5.5 MODIFICATION OF CARBONS BY NITROGEN SURFACE COMPOUNDS

The formation of carbon—nitrogen surface compounds and their influence on surface modification of carbons has been only sparsely reported, although it has been observed that the treatment of carbons with ammonia gas results in the formation of basic carbons which may have some applications. Boehm et al. (62) and Hofmann and Ohlerich (87) found that when an oxidized charcoal was heated with dry ammonia, nitrogen was bound to the surface. At low temperatures the fixation of nitrogen was equivalent to the number of acid groups as determined by sodium hydroxide neutralization capacity. This was attributed to the formation of ammonium salts. However, at high-temperature treatment a substitution of the hydroxyl groups by amono groups was postulated. The carbon became hydrophobic and markedly changed the adsorption capacity of the carbon for methylene blue, which is a basic dye (Table 27).

Puri and Mahajan (111) observed that the interaction of a sugar charcoal with dry ammonia gas involved neutralization of the surface acidic complexes and fixation of some additional amounts in nonhydrolyzable form. But they could not attribute this fixation of ammonia to any particular group on the carbon surface. However, Puri and Bansal (77) observed that when chlorinated sugar and coconut charcoals were treated with ammonia gas at 300°C, a part of the chemisorbed chlorine was evolved and substituted by amino groups.

Table 27 Reaction of Acid Surface Oxides with Ammonia (activated charcoal Carboraffin oxidized with HNO_3)

		Neutralization of:		
Reaction temperature (°C)	Nitrogen uptake (mg atom/ 100g)	KOH (alcoholic) (mEq/100 g)	NaOH (in H_2O) (mEq/100 g)	Adsorption of methylene blue (mg/g)
(untreated)	6	750	400	535
110	390	400	—	252
255	540	230	—	158
330	620	170	—	136
410	710	120	—	—

Source: Boehm et al. (62).

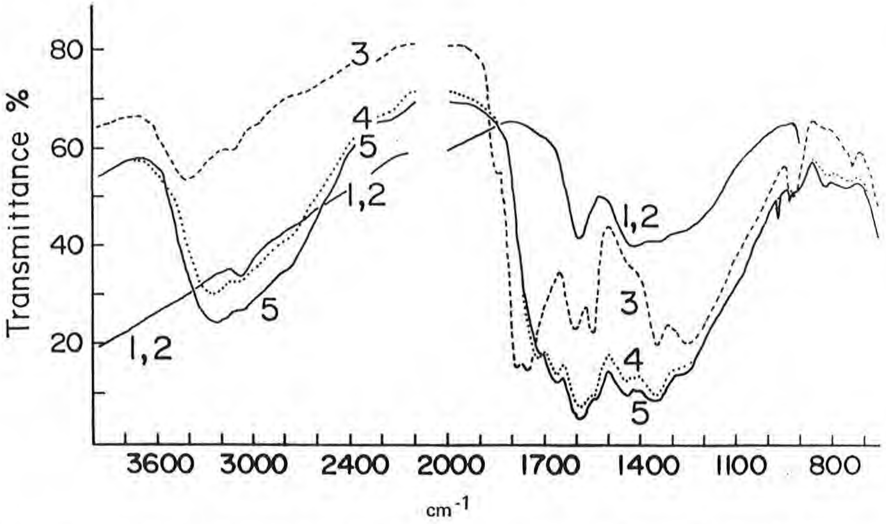


Figure 26 I.R. Spectra of ammonia sorbed on the surface of a carbonaceous film prepared from cellulose. (1) Cellulose carbonized at 400°C in CO_2 atmosphere (after desorption at 600°C). (2) Sorption of NH_3 at 1.5 kPa (1500 Pascal). (3) After oxidation in 63% aqueous HNO_3 (1 hr at 1000°C) and desorption at 200°C. (4) Sorption of NH_3 at 0.18 kPa. (5) Sorption of NH_3 at 1.5 kPa. (All spectra recorded in a vacuum cell, expansion 1.11.) [From Zawadski (112). Reproduced with permission from Pergamon Press.]

The resulting charcoals were basic in character and showed enhanced adsorption for acids. The increase in the acid adsorption corresponded to nitrogen fixed on treatment of the chlorinated charcoals with ammonia, indicating an exchange of C—Cl bond by a $C—NH_2$ bond (Table 21).

Zawadzki (112) treated a carbon film with ammonia gas before and after oxidation with nitric acid and using IR spectroscopy observed no adsorption of ammonia before oxidation of the film. However, the oxidation of the carbon film with nitric acid caused adsorption of ammonia, resulting in a sharp IR absorption in the N=H stretching vibration region. The three bands at 1840, 1780, and 1740 cm^{-1}, which were present in the oxidized film, disappeared on adsorption of ammonia and a single band in the region of C=O stretching vibrations at 1720 cm^{-1} was formed (Fig. 26). This band was attributed to imide structures. The disappearance of the doublet of bands 1840 and 1780 cm^{-1} was attributed to the reaction of ammonia with the cyclic anhydride structures and the disappearance of

Table 28 Irreversible Sorption of Ammonia on Surface of Carbonaceous Films

Kind of carbonaceous film	Quantity of NH_3 sorbed irreversibly after the desorption at room temperature (mmol/g)	Quantity of NH_3 sorbed irreversibly after the desorption at room temperature (mg/g)
Desorbed at 600°C	0.18	3.1
Desorbed at 600°C and oxidized with HNO_3	2.06	35.0
Desorbed at 800°C	0.37	6.3
Desorbed at 800°C and oxidized with HNO_3	1.75	29.7

Source: Zawadski (112). Reproduced with permission from Pergamon Press.

the 1740 cm^{-1} band to the interaction of ammonia with the lactone structures. The desorption experiments on the ammonia-treated oxidized carbon film showed that the bonded nitrogen was very stable. Oxidized carbon film could bind more than 10 times the amount of ammonia than could the unoxidized film (Table 28).

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concentration in the solution. However, Huang and Bowers (59) failed to confirm this observation. These workers (59) found that the adsorption and reduction were occurring simultaneously and were responsible for the removal of Cr(VI). They were able to calculate the rates of the two reactions. These workers also observed that when the carbon was oxidized with nitric acid and the solution containing (Cr(VI) with chlorine water, the removal of Cr(VI) was decreased considerably. This was attributed to the fact that these oxidations resulted in the chemisorption of appreciable amounts of oxygen enhancing the acidity of the carbon surface so that the carbon had greater affinity toward the reduced form of the metal Cr(III).

Yoshida et al. (65) observed that Cr(VI) was readily adsorbed by the activated carbon as anionic species such as $HCrO_4^-$ or CrO_4^{2-} while Cr(III) was scarcely adsorbed. They also found that the acidic solution of Cr(VI) was easily reduced to Cr(III) in the presence of carbon. The adsorbed Cr(VI) species could be recovered by washing with sodium hydroxide or hydrochloric acid solutions. The reduction of Cr(VI) into Cr(III) by activated carbon was also reported by Roersma et al. (66). The removal of chromate ions by activated carbon from aqueous solutions (67,68) was found to be a function of pH, the best pH range being acidic range pH 3–7.

6.13 ADSORPTION OF MERCURY ON CARBONS

The adsorption of Hg(II) from aqueous solutions using activated carbon was found to be pH dependent (69–71). The adsorption of Hg(II) increased as the pH of the solution was decreased, the acidic pH range being most suitable. Twice as much mercury was removed when the pH was decreased from 9 to the acidic range. Yoshida et al. (65,72) studied the use of several activated charcoals for the removal of Hg(II) and observed that the removal efficiency of a carbon depended on the nature of the carbon and the nature of the activation treatment that the carbon received. The carbons obtained from wood, coconut shells, and coal and activated in steam were found to have a high adsorption capacity for Hg(II) from solutions below pH 5. The ability decreased with increase in pH of the solution. The wood charcoal given a chemical activating treatment with zinc chloride was found to have a higher capacity for adsorption of Hg(II) even at pH greater than 5. The adsorption of $HgCl_4^{2-}$ in HCl medium was reversible both in the case of steam-activated and chemically activated carbons but at pH > 7 the steam-activated carbons showed irreversible adsorption accompanied by reduction of Hg(II) on the surface of the carbon. The efficiency of an activated carbon to adsorb Hg(II) was also enhanced by the addition of certain chelating agents (71) or by sulfurization of the carbon surface (73,74). Activated carbons modified by impregnation with cartain metallic sulfides were also found to be very efficient for selectively adsorbing Hg(II) from aqueous solutions (75,76).

Thiem et al. (70) observed that mercury can be removed from water using powdered activated carbons, the amount of removal depending upon the pH and the amount of charcoal (Fig. 28). Roughly twice as much mercury was removed at pH 7 as at pH 9. Increasing the hydroxyl ion concentration evidently reduced the adsorption of mercury by the carbon. The addition of chelating agents such as tannic acid or EDTA improved the adsorption of mercury. The addition of as little as 0.02 mg/L of the chelating agent increased the adsorption of mercury from 10 to 30% depending on the pH of the solution and the amount of the carbon used. Tannic acid was more effective (Fig. 29), whereas nitric acid showed minimum effect. The presence of calcium ions in water also improved the adsorption of mercury (Fig. 30). The mercury adsorption increased from 10 to 20% as

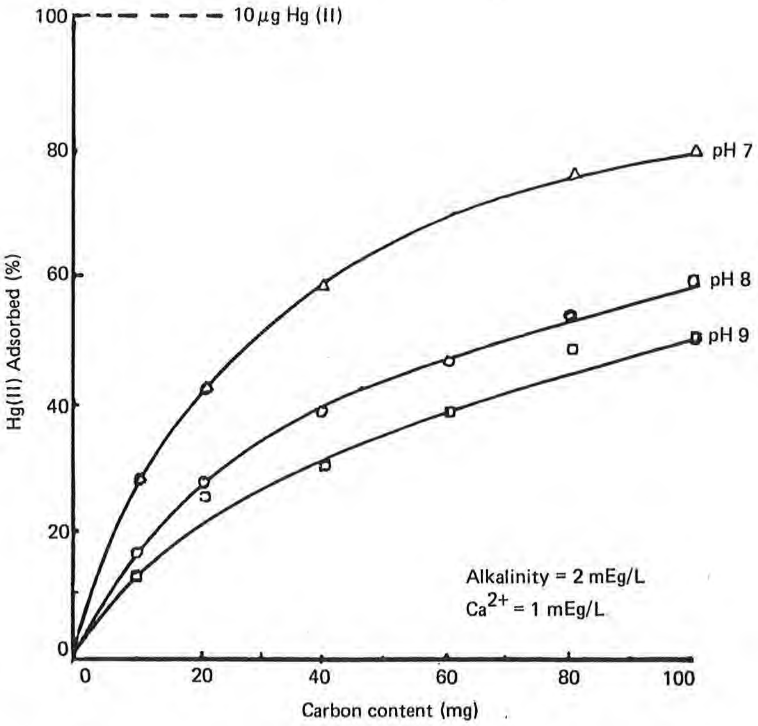

FIGURE 28 Removal of mercury as a function of carbon content at different pH values. [From Thiem et al. (70). Reproduced with permission from American Water Works Association.]

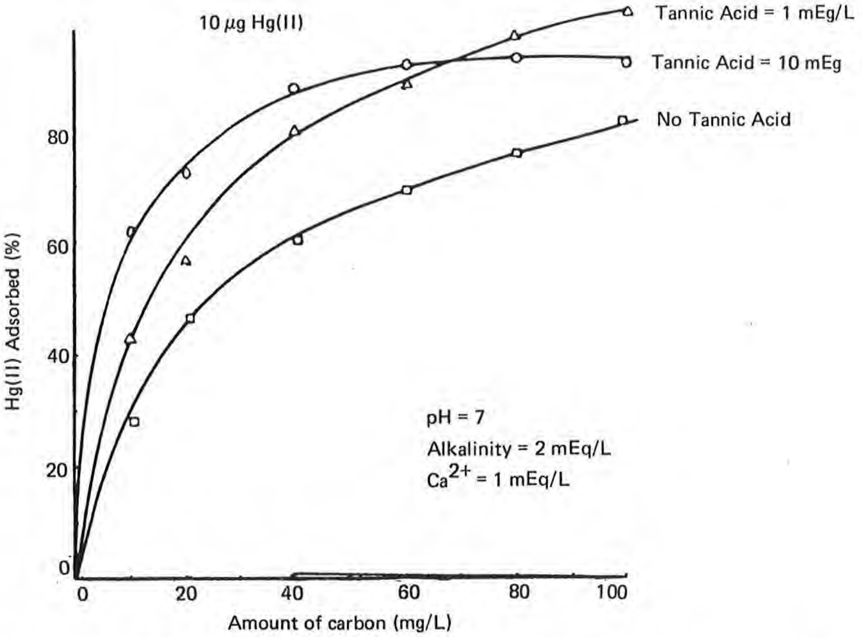

FIGURE 29 Influence of addition of tannic acid on the removal of mercury from aqueous solutions. [From Thiem et al. (70). Reproduced with permission from American Water Works Association.]

the calcium ion concentration was increased from 50 to 200 mg/L. When both calcium ions and tannic acid were present, the removal of mercury was almost doubled, even with smaller amounts of carbon.

Sinha and Walker (74) observed that sulfurized carbons could be used for the removal of mercury vapors from contaminated streams at 150°C. They sulfurized a Saran carbon to sulfur loadings varying between 1.0 and 11.8% by weight of sulfur by the oxidation of hydrogen sulfide on the carbon surface at 140°C in a fluidized bed. The mercury-contaminated airstream was passed through a bed of 1 g of the sulfur-loaded carbon with a contact time of 0.05 sec. The rate of mercury buildup in the effluent was extremely low when the mercury-contaminated stream was passed through the bed at 150°C (Fig. 31). This large capacity of the sulfurized carbon was attributed to the interaction between the mercury and the sulfur present on the carbon surface.

Ammons et al. (77) studied the adsorption of methyl mercuric chloride from aqueous solutions on Filtrasorb 200—activated carbon at room temperature and observed that the adsorption isotherms were nonlinear and did not fit either the Freundlich or the Langmuir isotherm. The adsorption was, however, reversible in nature.

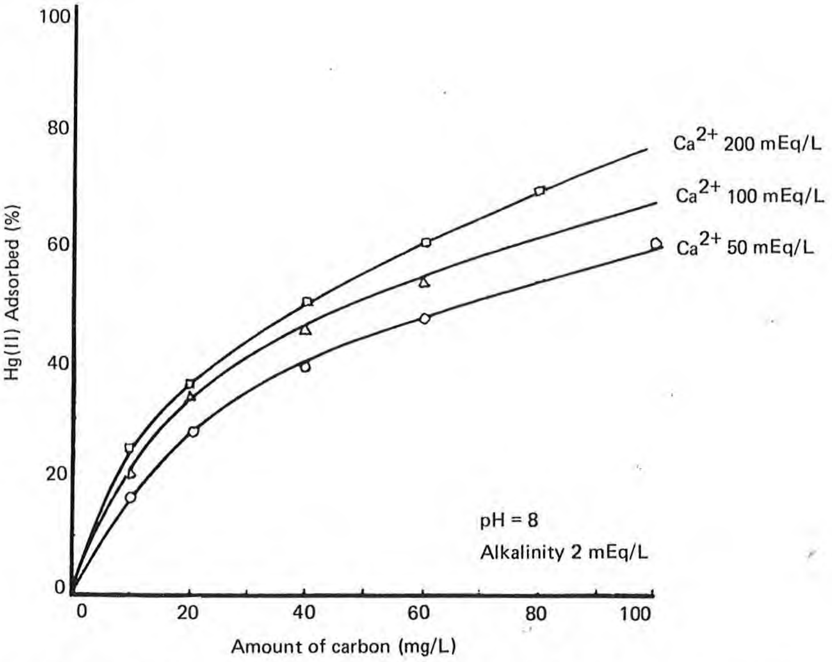

FIGURE 30 Effect of presence of calcium ions on the adsorption of mercury from aqueous solutions by carbon. [From Thiem et al. (70). Reproduced with permission from American Water Works Association.]

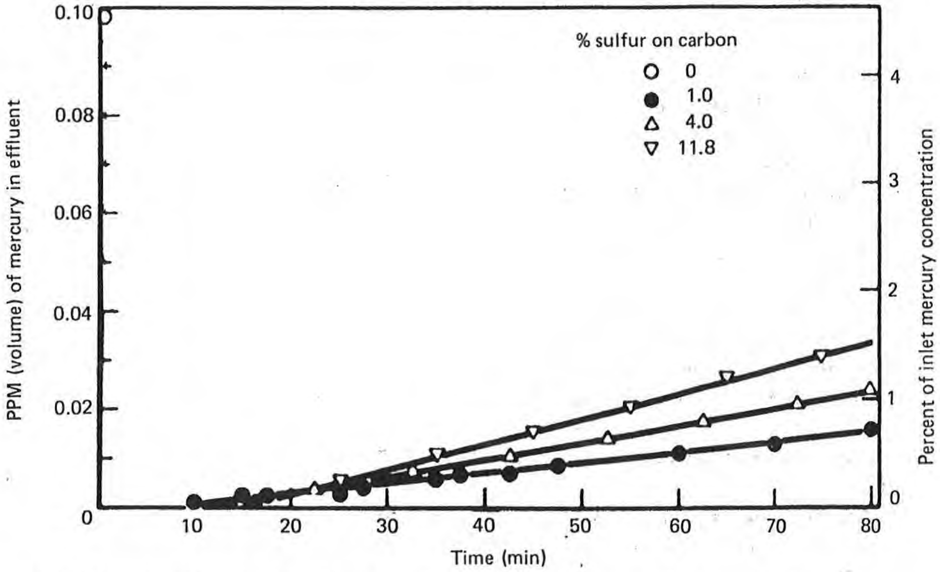

FIGURE 31 Effect of sulfur content in carbon on the removal of mercury vapors from air. [From Sinha and Walker (74). Reproduced with permission from Pergamon Press.]

6.14 REMOVAL OF COPPER BY ACTIVE CARBONS

Moore (78) studied the adsorption of Cu(II) from seawater desalination plant effluent using several different activated carbons. The adsorption isotherms were generally type I of the BET classification. The extent of adsorption was a function of the total Cu(II) concentration and pH of the solution as well as the nature of the carbon. The rate of adsorption at pH < 3 was very high in the initial stages, reached a maximum value, and then declined steeply. However, the adsorption at pH 3 increases very fast and then becomes asymptotic after a few minutes (Fig. 32). The maximum in the adsorption at pH < 3 was attributed to the instantaneous precipitation of the solid copper hydroxide on the carbon surface during which the pH of the system became alkaline. The adsorption then decreased as a result of the slow release of Cu(II) ions into the solution. The adsorption of Cu(II), however, was small, never reaching more than 6%. The treatment of the carbons with organic chelating agents increased adsorption but only slightly. Nelson et al. (79) observed that the adsorption of Cu(II) from solutions containing varying concentrations of sodium chloride depended on the ionic strength of the solution. The adsorption increased by about seven times when the concentration of sodium chloride in the solution was increased from 0.1 to 6 *M*. This rapid increase in adsorption was attributed to the adsorption of the negatively charged CU(II) chloride complexes.

6.15 ADSORPTION OF VANADIUM ON ACTIVE CARBONS

The adsorption of V(IV) and V(V) by activated carbons has also been reported (80,81). The adsorption has been found to be sensitive to the pH of the solution and the nature of the carbon surface. The adsorption of both V(IV) and V(V) increased with pH and was maximum in the pH range between 2.5 and 3 and was decreased thereafter. The oxidized charcoals generally showed more adsorption capacity toward both V(IV) and V(V). Kunz et al. (80) studied the adsorption from sodium metavanadate solution using Filtrasorb 400–activated carbon and observed that about 90% of the vanadium could be removed from a solution containing 50 mg/L. The efficiency of the carbon was improved when larger quantities of the carbon were used (Fig. 33).

6.16 REMOVAL OF ORGANICS FROM WATER BY ACTIVE CARBONS

More than 700 specific organic chemicals have been identified in drinking waters. These organics are derived from industrial and municipal discharge, urban and rural runoff, natural decomposition of vegetable and animal matter, as well as from water and wastewater chlorination practices. Considerable amounts of halomethanes—specifically—chloro-

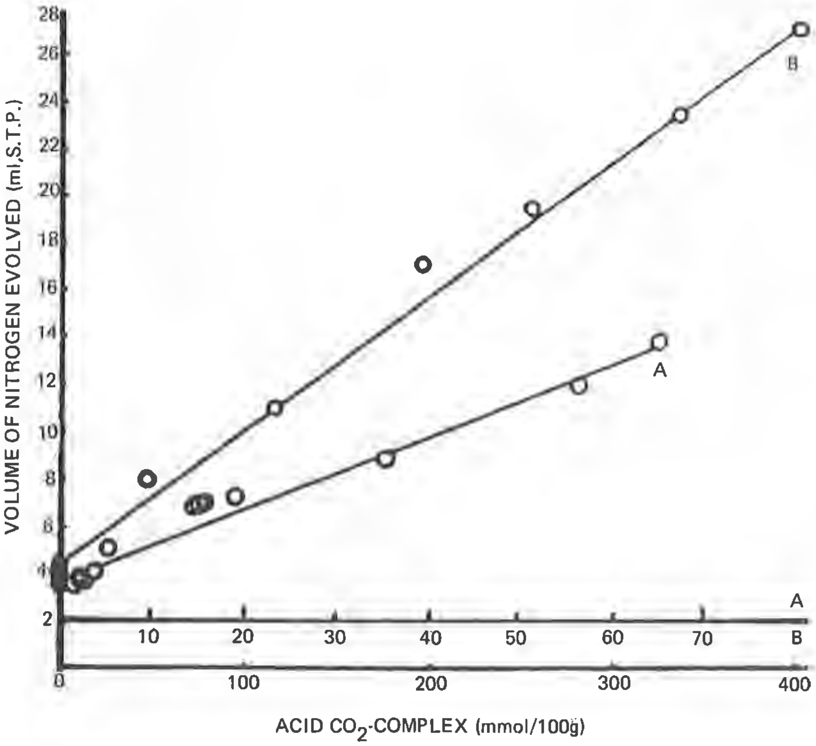

FIGURE 58 Relationship between acidic CO_2-complex and the catalytic activity of the carbon for sodium azide—iodine reaction. [From Puri et al. (151).]

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Printed in the United States of America

ISBN: 0—8247—7842—1

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