Surface-Treated Activated Carbon for Removal of Phenol from Water

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Abstract

Adsorption of phenol from dilute solutions has been studied on porous and nonporous carbons, as well as on ion-exchange resins. At a given equilibrium concentration, uptake of phenol on nonporous carbons per unit area is determined by the nature of the carbon surface. Phenol uptake on porous activated carbons decreases sharply upon surface oxidation. However, progressive elimination of chemisorbed oxygen from the oxidized carbon upon heat treatment at increasing temperatures in N_2 increases the phenol adsorption capacity. The capacity is further enhanced if following heat treatment in N_2 at 950°C the samples are reacted with H_2 at 300°C. The mechanism of phenol adsorption on carbons has been discussed. Activated carbons are more effective adsorbents for phenol than commercial ion-exchange resins.

INTRODUCTION

Recent EPA and PHS studies have shown the presence of several carcinogenic organics in drinking waters in many cities in the United States. Because of its large surface area, activated carbon is a potential adsorbent for the removal of organics. However, there is now a growing realization that surface area of an activated carbon cannot be used as a single criterion of its adsorptive capacity because, in many cases, it is

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the nature of the carbon surface and not its magnitude which determines its adsorption characteristics (*1*, *2*). In the present study we have investigated the use of surface-modified carbons for the removal of phenol from water.

EXPERIMENTAL

Adsorbents

Activated carbons supplied by six different companies were used in the present study. They have been designated Carbons A through F. Carbons A through E are granular carbons which are in commercial production. They were used in our recent studies on removal of ammonia from water (*2*). Carbon F is a powdered carbon which is not yet available in commercial amounts. It became available to us late in this research program, but was of interest because of its large surface area. Two carbon blacks, Spheron-6 (a channel black) and Vulcan-3 (a furnace black), supplied by Cabot Corp., were used before and after graphitization at 2800°C. The graphitized samples are referred to as Graphon and V3G, respectively, in the text. Graphitization was carried out in the manner described previously (*3*). Saran carbon, prepared by carbonizing Saran (a copolymer of PVDC and PVC in the ratio of 9:1) at 950°C (*4*), as well as a sample of polycrystalline graphite, before (G) and after (GB) doping substitutionally with 0.79 wt-% boron in the manner described elsewhere (*5*), were also used. Two ion-exchange resins, Ambersorb XE-347 and Ambersorb XE-348, obtained from Rohm and Haas, were also used as adsorbents.

Surface Area

Surface areas of various adsorbents measured from N_2 (77 K) and/or CO_2 (298 K) isotherms using the BET and Polanyi-Dubinin equations, respectively (*6*), are listed in Table 1. For each activated carbon, N_2 surface area is significantly higher than the corresponding CO_2 area. This has previously been reported to be due to the presence of small pores in which reversible capillary condensation of N_2 occurs at very low relative vapor pressures before the apparent monolayer capacity is attained (*7*). It is now generally agreed that CO_2 adsorption at 25°C measures more or less closely the total surface area of microporous carbons (*8*).

Surface Oxidation

Selected carbons were given oxidative treatments with HNO_3 (10 mL/g)

TABLE 1

Surface Areas of Adsorbents

Adsorbent	Mesh size	Surface area (m^2/g)	
		CO_2	N_2
Activated carbons:			
A	12×40	836	975
B	4×10	540	945
C	8×30	566	835
D	6×8	566	890
E	4×10	799	902
F	-200	1360	1640
Saran carbon:	40×70	1170	901
		1190	1370
Activated to 31% burn-off			
Carbon blacks:			
Spheron-6	—	—	116
Graphon	—	—	80
Vulcan-3	—	—	77
V3G	—	—	60
Graphite:			
G	-100	—	4.6
GB	-100	—	4.7
Ion-exchange resins:			
XE-347	20×50	—	400
XE-348	20×50	—	550

and saturated ammonium persulfate $[(NH_4)_2S_2O_8]$ in $2 N$ H_2SO_4 in the manner described previously (2).

Treatment with Ammonia

Carbon was heated up to 500, 700, and 900°C in a flow of dry NH_3 gas at a heating rate of 10°C/min; soak time at the maximum temperature in each case was 2 h. Following heat treatment, NH_3 was replaced by N_2. The sample was cooled down to room temperature in N_2 and then washed free of adsorbed ammonia with hot distilled water. The treated sample was dried in a vacuum oven at 110°C. Nitrogen contents of the samples were measured using the Carlo-Erba Elementary Analyzer No. 1106.

Adsorption of Phenol

About 0.1–0.5 g portions of adsorbents were mixed with 100 mL of aqueous phenol solution in the concentration range 0.1–10.0 mmol/L. The suspensions were shaken mechanically for 48 h after which the decrease in phenol concentration was measured by UV spectrophotometry

at 270 mμ. It was ascertained in a few preliminary runs that equilibrium was attained well within 48 h.

RESULTS AND DISCUSSION

Activated carbons usually have a trimodal distribution of pore sizes, namely macropores, mesopores, and micropores. Pores larger than 50 nm in diameter are classified as macropores, pores with sizes between 2–50 nm are known as mesopores, and pores smaller than 2 nm are termed micropores. Some of the micropores in activated carbons may be commensurate in size with those of the adsorbate molecules. As a result, the surface area located in such pores may not be accessible for adsorption. In adsorption studies, particularly those from the solution phase, it is not uncommon that the size of the adsorbate molecule is different from that of the molecule used for measuring the surface area of the adsorbent. This situation can lead to misleading conclusions when different microporous carbons are evaluated and compared with respect to adsorption capacity for a specific adsorbate per unit area. Therefore, to delineate unambiguously the importance of the magnitude of the surface area as well as the nature of the carbon surface on adsorption characteristics, it is imperative that the extent of adsorption per unit area be considered for nonporous carbons and/or carbons devoid of ultramicroporosity. Thus adsorption of phenol was first studied on two carbon blacks, namely Spheron-6 and Graphon.

Graphon is essentially nonporous; its surface is composed almost entirely of the basal planes of carbon crystallites (9). Almost 90% of the BET surface area of Spheron-6 is accounted for by its geometric area as measured by electron microscopy (10). Further, this carbon black does not contain pores smaller than 0.7 nm in width (11). That is, pores in Spheron-6 are larger in size than the minimum dimension of a phenol molecule. Graphon and Spheron-6, however, differ in the nature of their surface. For example, Spheron-6 has an oxygen content of about 3%, which on high temperature evacuation is desorbed as H_2O, CO, and CO_2 (1), whereas Graphon is essentially free of oxygen complexes. As a result, an aqueous suspension of Spheron-6 has an acidic surface (pH < 7) whereas Graphon gives an alkaline suspension (pH > 7).

Adsorption isotherms of phenol on Spheron-6 and Graphon are plotted in Fig. 1. In order to eliminate the effect of different surface areas of the two carbon blacks, uptake of phenol is expressed per unit area of the adsorbent. At lower concentrations, Spheron-6 adsorbs significantly more phenol than Graphon. This trend is reversed at higher concentrations. These results demonstrate clearly that the nature of the carbon surface can have an important effect on phenol uptake.
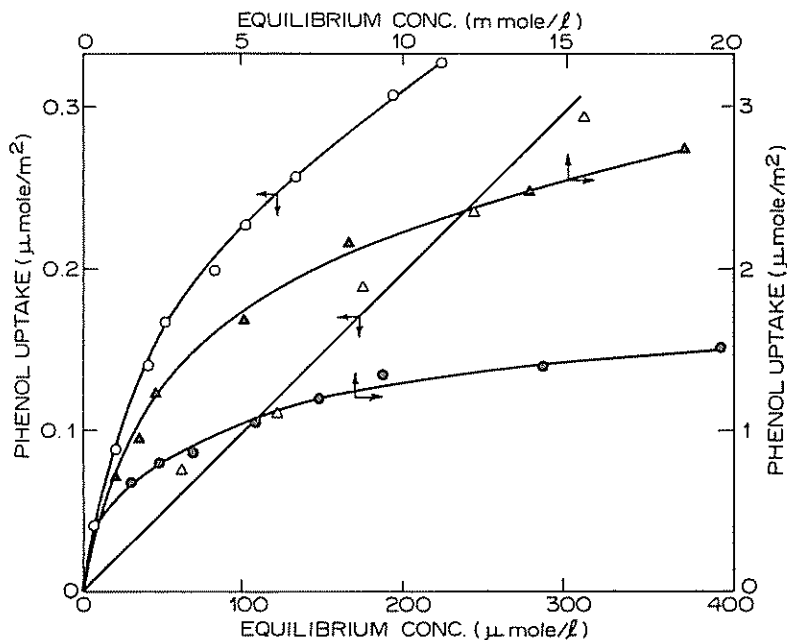
FIG. 1. Phenol adsorption isotherms from aqueous solution on Spheron-6 (O, ⊚) and Graphon (△, ▲).

The linear dependence of phenol uptake on the concentration observed for Graphon at lower concentrations is rather an unusual feature of adsorption from solution. This behavior is analogous to obeyance of Henry's law for adsorption of gases at low pressures on homogeneous carbon surfaces (*12, 13*). Reasons for higher phenol uptake on Graphon at higher concentrations will be discussed later in this paper. However, at this stage we are unable to explain unequivocally the higher uptake of phenol on Spheron-6 at lower concentrations. Spheron-6 and Graphon differ from each other not only in the amount of oxygen complexes but also in the energetics of their surfaces. Graphon has essentially a homogeneous surface composed of (00*l*) planes whereas the surface of Spheron-6 is heterogeneous in nature; that is, composed of both (00*l*) and (100) planes (*14*). Adsorption of gases on heterogeneous carbon surfaces at low pressures is characterized by a higher heat of adsorption than that on a homogeneous surface (*15*). At low surface coverages the higher heat of adsorption can lead to a higher uptake of adsorbate per unit area (*16*). Whether this phenomenon holds for adsorption from the solution phase is open to speculation.

Results similar to those for Spheron-6 and Graphon were also observed for the other two carbon blacks used in this study, namely Vulcan-3 and V3G.

Adsorption of phenol was next studied on the as-received commercial activated Carbons A, B, C, D, and E. These carbons adsorb significant amounts of phenol over the entire range of concentrations studied (Table 2). Data points in Table 2 were computed from the respective adsorption isotherms. These results show that the extent of phenol uptake is not necessarily determined by the total surface area (as measured by CO_2) alone. For instance, Carbon D, which has a lower N_2 and CO_2 area than Carbons A and E (Table 1), has somewhat higher adsorptive capacity for phenol. This could be due to two reasons. First, Carbons A and E may contain a larger proportion of smaller pores than Carbon D, which may be accessible to the smaller CO_2 molecule but may not be accessible to the larger phenol molecule. Second, depending upon the nature of the organic precursor used for producing activated carbon, the amount and nature of inorganic impurities present, and the activation process and degree of activation used, different carbons are expected to have different surface properties and surface characteristics which, as will be discussed shortly, can have a profound effect on the adsorption phenomenon.

Results given in parentheses in Table 2 show that phenol uptake decreases somewhat upon treatment of as-received activated carbons with HCl. The treatment is expected to remove, at least partly, the inorganic impurities either present initially in the organic precursor used for the production of activated carbon or added during the activation step (2). Possible reasons for this behavior will be discussed later in this paper.

For each activated carbon, phenol uptake was found to decrease appreciably upon surface oxidation with HNO_3 or $(NH_4)_2S_2O_8$. In each

TABLE 2

Phenol Uptake on As-Received and Acid-Treated Activated Carbons

Carbon	Phenol uptake (mmol/g) at equilibrium concentration (mmol/L)							
	0.05	0.15	0.25	0.40	1.0	2.0	4.0	8.0
A	0.74	1.18	1.32	1.45	1.84	2.11	2.44	2.76
	(0.75)	(1.13)	(1.28)	(1.42)	(1.74)	(2.03)	(2.38)	—
B	0.75	1.01	1.15	—	—	—	—	—
C	0.70	1.04	1.17	1.26	1.57	1.76	1.94	2.26
D	0.77	1.18	1.35	1.55	1.92	2.34	2.72	3.06
	(0.70)	(1.11)	(1.29)	(1.50)	(1.82)	(2.14)	(2.55)	—
E	0.81	1.08	1.27	1.50	1.82	2.10	2.46	2.76
	(0.61)	(0.94)	(1.09)	(1.25)	(1.58)	(1.84)	(2.23)	—

case the oxidative treatment increased the acidity of the carbon surface (2). Because of reasons of space, results for only one commercial activated carbon, namely Carbon A oxidized with $(NH_4)_2S_2O_8$, are being reported. Results plotted in Fig. 2 bring out clearly the marked retarding effect of oxygen complexes on phenol uptake. For example, at an equilibrium concentration of 0.10 mmol/L, the fully oxidized sample adsorbs only one-tenth the amount of phenol which is adsorbed by the as-received carbon. As the oxidized sample is heated in N_2 at progressively increasing temperatures, increasing amounts of oxygen complexes are desorbed and concomittantly surface acidity decreases (Table 3). As surface acidity decreases, phenol uptake increases. It is noteworthy that after heat treatment at 950°C, the oxidized sample attains more or less the same adsorptive capacity as the as-received carbon, even though its surface area as measured by CO_2 and N_2 adsorption has been significantly reduced over that of the as-received sample.

Surface areas of Carbon A after surface oxidation with $(NH_4)_2S_2O_8$ as well as following heat treatment of the oxidized carbon at different temperatures are listed in Table 3. Surface oxidation brings about a sharp decrease in both N_2 and CO_2 areas. Heat treatment of the oxidized carbon up to 500°C increases the CO_2 and N_2 areas. An increase in HTT (heat treatment temperature) from 500 to 700°C decreases the areas. Further
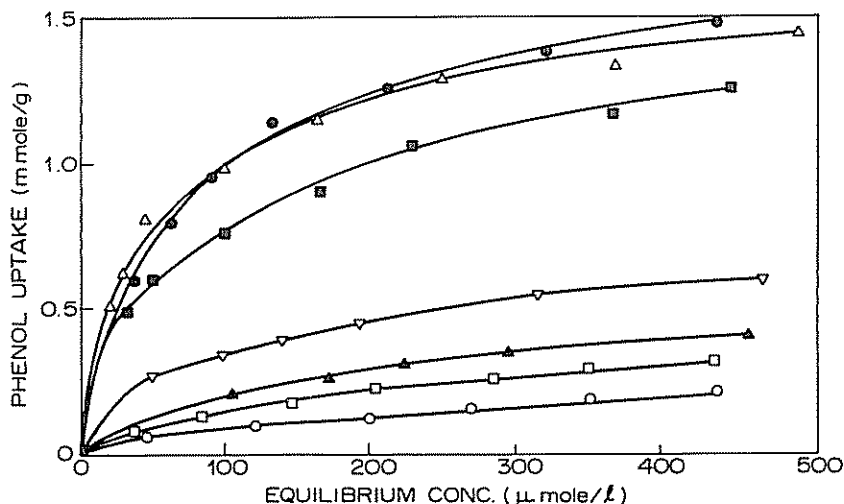

FIG. 2. Phenol adsorption isotherms from aqueous solution on various carbon A samples: (⊕) as-received; (○) as-received oxidized with $(NH_4)_2S_2O_8$. Oxidized carbon heat treated in N_2: (□) 300°C; (▲) 400°C; (▽) 500°C; (▣) 700°C; (△) 950°C.

TABLE 3

Surface Areas and Surface Acidities of Carbons

Sample	Surface area (m^2/g)		Surface acidity (meq/g)
	CO_2	N_2	
Carbon A:			
As-received	836	975	0.12
As-received HT in N_2 at 950°C	1014	1029	Nil
As-received oxidized with $(NH_4)_2S_2O_8$	545	503	5.93
Oxidized and heat treated at (°C):			
300	565	620	4.79
400	617	606	2.74
500	657	681	1.60
700	580	640	0.34
950	572	675	Nil
Saran carbon:	1170	901	—
activated to 31% burn-off	1190	1370	—
Activated Saran carbon oxidized with HNO_3	1224	—	—
Spheron 6	—	116	—
Spheron 6 HT at 600°C	—	119	—

increase in HTT from 700 to 950°C has essentially no effect on CO_2 and N_2 areas. Some of the observed changes in phenol uptake in Fig. 2 may partly be due to changes in surface area. It is noteworthy that even though the 700°C heated sample has a lower CO_2 area than the 500°C heated sample, the former has a much higher adsorption capacity for phenol. Furthermore, the 700 and 950°C heat treated samples have about the same N_2 and CO_2 areas, yet the latter sample adsorbs significantly more phenol over the entire concentration range.

It is realized by the authors that the results presented in Fig. 2 do not show unequivocally the relative importance of surface area and nature of carbon surface in influencing phenol uptake. In order to overcome this drawback, it was thought desirable to use carbons devoid of ultramicroporosity. Therefore, phenol adsorption was next studied on an activated Saran carbon and Spheron-6 samples. Saran carbon is highly microporous and most of the area is enclosed in pores 0.55 to 0.60 nm in width (17, 18). This carbon was activated to enlarge its pore size in the following manner. The carbon was heated in N_2 up to 950°C at a heating rate of 10°C/min; soak time at 950°C was 2 h. This thermal treatment would more or less completely desorb surface oxygen complexes (1). Following HT, the sample was cooled in N_2 down to 200°C, at which stage N_2 was replaced by air. Reaction with air was carried out for 6 h. It is believed that under these conditions dissociative chemisorption of oxygen on "active" carbon

sites will be more pronounced than gasification of the carbon matrix. Following the oxidation step, air was replaced by N_2 and the sample was once again heated up to 950°C (in the manner discussed above) to desorb oxygen complexes. The above HT cycle (chemisorption of oxygen at 200°C followed by desorption of oxygen complexes at 950°C) was repeated 35 times, at the end of which the cumulative weight loss during activation amounted to 31 %. We believe that for a given level of activation the mild activation conditions used in the present study would maximize pore enlargement and that the decrease in particle size resulting from external burn-off would be minimal. The activation process has essentially no effect on the CO_2 area, whereas the N_2 area increases by over 50 % (Table 3), indicating enlargement of pores to an extent where reversible capillary condensation of N_2 can occur (7). The activated Saran carbon was given surface oxidative treatments with H_2O_2 (2 N), HNO_3 (10 mL/g), and $(NH_4)_2S_2O_8$ (saturated solution) in the manner described elsewhere (2). It is reasonable to assume that because of the pore enlargement in activated Saran carbon, the deleterious effect of surface oxidation on its surface area would be less than that observed with the as-received commercial activated carbons. This is supported by the fact that there is little or no
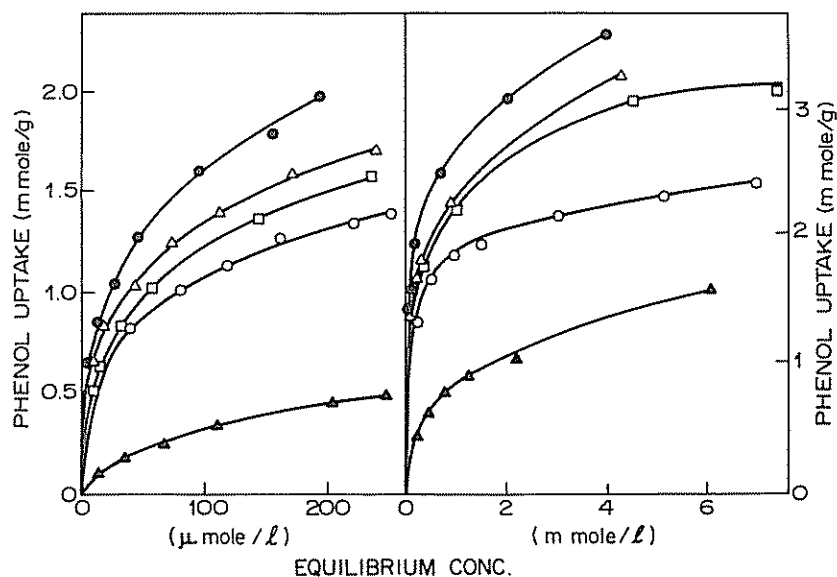

FIG. 3. Phenol adsorption isotherms from aqueous solution on various Saran carbon samples: (○) unactivated; (●) activated. Activated sample oxidized with: (△) H_2O_2; (□) $(NH_4)_2S_2O_8$; (▲) HNO_3.

change in the total (that is CO_2) area of the activated Saran carbon following oxidation with HNO_3 (Table 3).

Phenol adsorption isotherms, plotted in Fig. 3, show that even though the unactivated and activated Saran carbons have about the same CO_2 areas, the latter sample adsorbs significantly more phenol over the entire concentration range. These results suggest that some of the pores in the unactivated Saran carbon are not accessible to phenol molecules and that accessibility increases upon activation due to pore enlargement. Surface oxidation of the activated sample in each case brings about a marked decrease in phenol uptake (Fig. 3). The more marked the decrease in pH of an aqueous suspension of the activated carbon, as a result of activation, the more marked is the reduction in phenol uptake. That is, the lowering of pH is as follows: $HNO_3 > (NH_4)_2S_2O_8 > H_2O_2$ (2).

The effect of the nature of the carbon surface on phenol uptake was studied for Spheron-6 in an indirect manner. That is, the carbon was not given an oxidative treatment to increase its oxygen content, but rather its oxygen content was reduced by HT in N_2 up to 600°C (1). The HT has essentially no effect on surface area (Table 3). Adsorption isotherms plotted in Fig. 4 show that phenol uptake increases upon HT (that is, decrease in oxygen content).
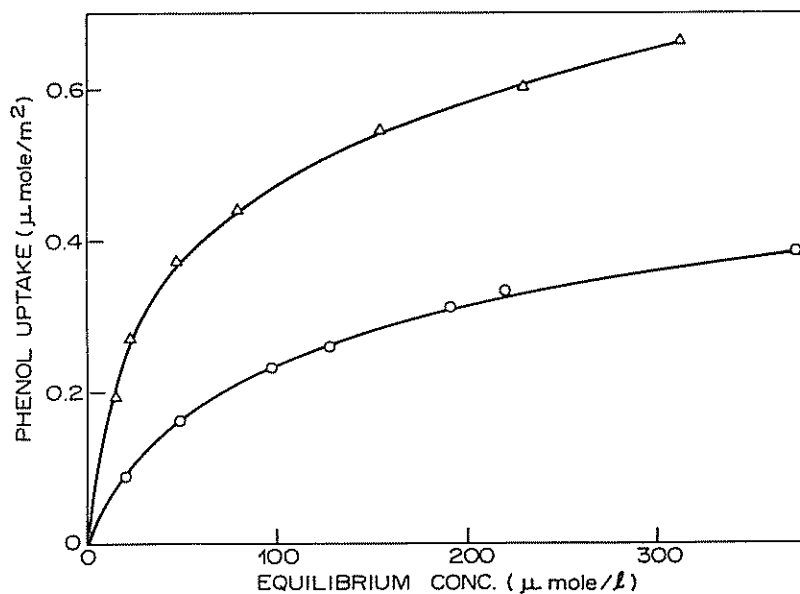

FIG. 4. Phenol adsorption isotherms from aqueous solution on Spheron-6 samples: (○) as-received; (△) heat treated in N_2 at 600°C.

Results of the present investigation thus show clearly that the nature of the carbon surface does influence phenol uptake. We have earlier reported that surface oxidation of carbon promotes uptake of ammonia from an aqueous solution (2). In contrast, results of the present study show that oxygen complexes decrease phenol uptake from water. These results emphasize the importance of the nature of the carbon surface in influencing adsorption behavior of carbons.

Coughlin et al. (19) have suggested that phenol adsorption on carbons involves dispersive forces between the π-electrons in phenol and the π-electrons in carbons. They attribute their finding that phenol adsorption decreases with increasing loading of oxygen complexes on carbons to removal of electrons from the π-band of carbon as a result of complex formation. Direct support for this view comes, perhaps for the first time, from our study of phenol adsorption on graphite and boron-doped graphite samples. Because of the relatively low surface areas of these samples (Table 1), phenol uptake was studied from very dilute solutions to assure a measurable change in concentration as a result of adsorption. Results plotted in Fig. 5 show that the addition of boron substitutionally into the lattice of polycrystalline graphite, with an accompanying removal
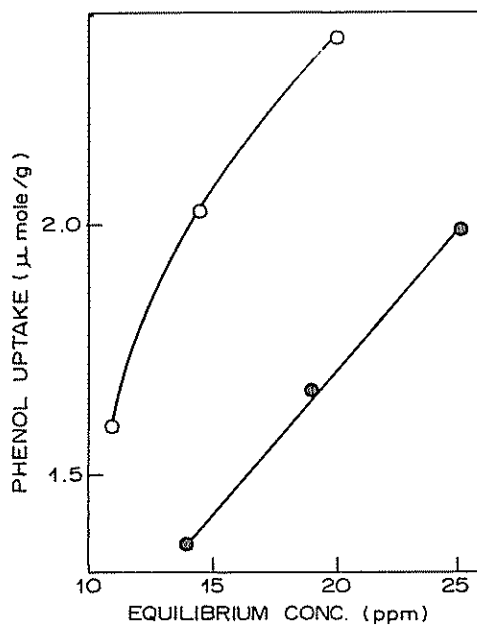

FIG. 5. Effect of substitutional boron in polycrystalline graphite on pheno uptake: (O) graphite; (●) graphite doped with 0.79% boron.

of π-electrons from the graphite, results in a lowering of phenol uptake from water. The decrease in phenol uptake upon acid treatment (Table 2) could possibly be due, at least in part, to the presence of some electron-donating impurities in the as-received carbons.

Mattson et al. (20) have suggested that phenol adsorption on carbons occurs by a donor-acceptor complex mechanism involving carbonyl oxygen on the carbon surface acting as the electron donor and the aromatic ring of phenol as the acceptor. In order to explain the results of Coughlin et al. (19), they suggest that the oxidation of the carbon surface increases the amount of strongly acidic oxygen containing functional groups through the oxidation of the carbonyl groups. As a result, the capacity of carbon for accepting electrons decreases. In this context it is noted that the extensive work of Puri does not substantiate the view that, upon oxidation, carbonyl oxygen groups become oxidized to carboxylic acid groups (1). It is well known that upon high temperature outgassing of oxygenated carbons, carbonyl groups evolve CO while carboxylic acid groups evolve CO_2 (1). Puri and Sharma have shown that surface oxidation of carbons and carbon blacks with various oxidizing solutions always increases the concentration of CO_2-evolving complex(es) but the CO-evolving complex either increases or remains essentially unchanged (21). In a previous study we oxidized some of the as-received activated carbons used in the present work with $K_2S_2O_8$, HNO_3, H_2O_2, and air (1). Some of these samples were available from the previous study. These samples were outgassed at 110°C (to remove physically adsorbed water) in vacuum and then heated slowly up to 950°C. In order to avoid the possibility of a reaction between evolved CO_2 and carbon substrate, CO_2 was frozen using a liquid N_2 trap. At the end of the run, the concentration of CO and CO_2 was measured mass spectrometrically. Results listed in Table 4 are consistent with the findings of Puri et al. (1). That is, in each case both CO_2- and CO-evolving complexes increase upon surface oxidation.

It may be argued that phenol can form H-bonds with the polar oxygen centers on the carbons. If it were so, phenol uptake should increase with surface oxidation of the carbons. This is contrary to the results obtained in this study (Fig. 2). It is suggested that oxygen chemisorbed on the carbon surface provides sites at which preferential uptake of water (over phenol) occurs; the adsorbed water molecules act as secondary sites and H-bond to other water molecules leading to the formation of clusters or islands (1). Since the carbon surface competes for both phenol and water molecules, preferential uptake of water on oxygenated sites could result in an increase in phenol concentration in the solution. That is, uptake of phenol on carbon would tend to decrease its concentration in the solution whereas preferential uptake of water would tend to increase the phenol

TABLE 4

Desorption of Oxygen Complexes upon Outgassing at 950°C

Sample	Gases evolved (meq/g)	
	CO_2	CO
Carbon C		
Acid treated	0.57	1.15
Acid treated oxidized with:		
Air	0.92	3.22
$K_2S_2O_8$	1.03	1.58
HNO_3	3.52	3.60
Carbon D		
Acid treated	0.57	0.81
Acid treated oxidized with:		
H_2O_2	0.77	1.10
$K_2S_2O_8$	0.79	1.35
HNO_3	4.16	4.16

concentration. The net result would be a relatively smaller decrease in phenol concentration as a result of the adsorption phenomenon. This would be reflected in a lower uptake of phenol. Alternatively, it is possible that a part of the surface covered by water molecules may either not be available for phenol adsorption or may cause a decrease in interaction energy between phenol molecules and the carbon surface. Both these factors could decrease the extent of phenol uptake. In the case of oxidized porous carbons, water clusters or islands possibly can also block entrances to some of the aperture-cavity pores, thus decreasing phenol uptake.

The mechanism suggested above receives support from the fact that phenol uptake decreased when H^+ ions of carboxylic acid present on the surface of Carbon D oxidized with $(NH_4)_2S_2O_8$ (surface acidity of the oxidized carbon was 3.95 meq/g) were exchanged with Na^+ ions (Fig. 6). This exchange was effected by contacting 1 g oxidized carbon with 100 mL of 0.1 N NaHCO$_3$ solution for 24 h, followed by removal of excess alkali by washing with a 60% alcohol–40% water mixture. The amount of exchangeable Na^+, determined by contacting the exchanged sample with 0.1 N HCl for 24 h followed by measuring the decrease in acid concentration, was found to be 1.62 meq/g. The decrease in phenol uptake observed upon replacement of surface H^+ ions by Na^+ ions (Fig. 6) appears to be consistent with the observation of Puri and Mahajan that oxygen-containing carbons with exchangeable metal cations adsorb more water than the unexchanged samples (22).

Based on the foregoing discussion, it is reasonable to suggest that the presence of oxygen complexes will favor phenol uptake from a nonpolar
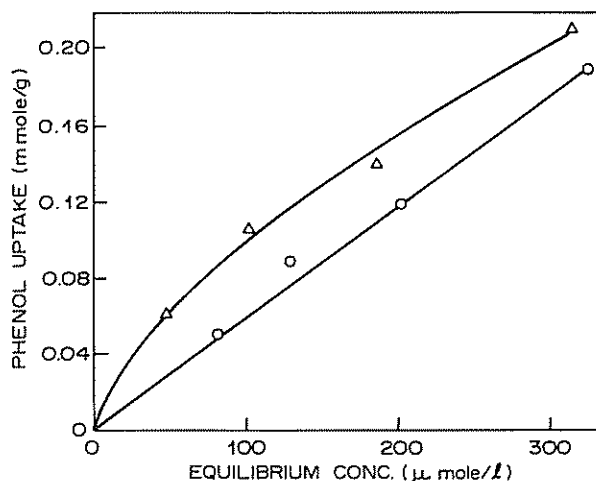
FIG. 6. Effect of exchangeable Na^+ ions on phenol uptake from aqueous solution on oxidized carbon D: ($\triangle$) oxidized; ($\bigcirc$) Na^+-exchanged.

medium by a mechanism involving H-bonding. In order to see if such is the case, phenol uptake was next studied on two carbon samples varying significantly in their surface acidities. These samples were prepared by heat treatment of $(NH_4)_2S_2O_8$ oxidized Carbon A in N_2 at 300 and 400°C. The two carbons, as indicated in Table 3, have surface acidity values of 4.79 and 2.74 meq/g, respectively. Adsorption isotherms for phenol uptake from cyclohexane solution are plotted in Fig. 7. It is noteworthy that the 300°C heat-treated carbon adsorbs somewhat more phenol than the 400°C heat-treated carbon. This trend is opposite to that observed for adsorption from aqueous solution (Fig. 2). Since the minimum dimension of a cyclohexane molecule is larger than that of a water molecule, it is possible that the larger cyclohexane molecule may be excluded from some of the micropores in the two carbons which may be accessible to smaller water molecules. As a result, some of the micropores may be available for phenol adsorption from aqueous solution but not from the cyclohexane solution. In order to circumvent this problem, it is desirable to express the magnitude of phenol adsorption per unit surface area measured by cyclohexane adsorption. The BET cyclohexane areas (measured at 20°C) for the 300 and 400°C heat-treated samples were 420 and 500 m^2/g, respectively. These areas are significantly lower than the corresponding CO_2 and N_2 areas (cf. Table 3), indicating the presence of some micropores in the two carbons which are inaccessible to cyclohexane. When adsorption of phenol per unit cyclohexane area is plotted for the 300 and 400°C
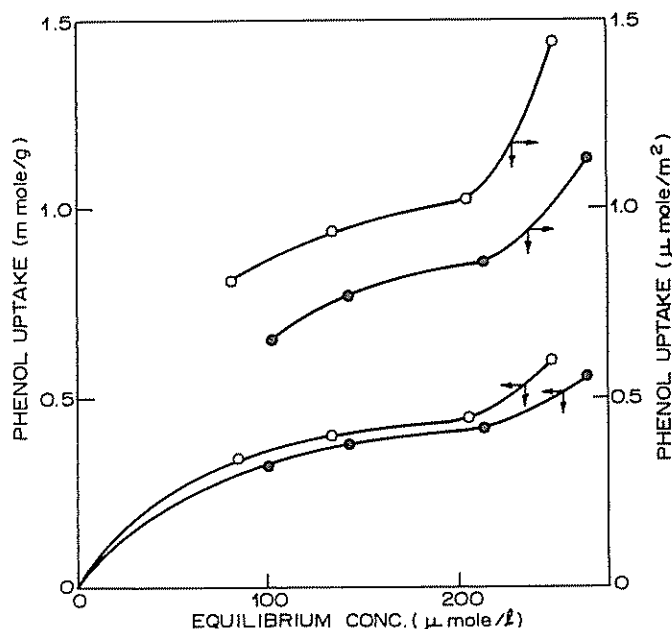
FIG. 7. Effect of oxygen complexes on carbon A samples upon phenol uptake from cyclohexane solution. Oxidized carbon heat treated in N_2: (O) 300°C; (◉) 400°C.

heat-treated carbons (Fig. 7), the former sample is seen to adsorb significantly more phenol relative to the latter sample. These results bring out clearly the beneficial effect of oxygen complexes on phenol uptake from a nonpolar medium. This effect is manifested most probably through hydrogen bonding between phenol and polar oxygen centers on carbons.

Phenol adsorption capacity of as-received activated carbons was found to increase significantly following HT in N_2 up to 950°C. Results for selected samples are plotted in Fig. 8. The increase was found to be a maximum for Carbon F. In this case, HT increases phenol uptake by a factor of over two. The increase cannot be attributed to an increase in surface area as a result of HT. HT of Carbon F to 950°C produced CO_2 and N_2 surface areas of 1360 and 1614 m²/g, compared to 1360 and 1640 m²/g for the original sample. In this context, HT of Carbon A to 950°C increases the CO_2 area appreciably whereas the N_2 area increases only slightly (Table 3). It is noteworthy that the relative increase in phenol uptake is far more pronounced than the corresponding increase in total (that is, CO_2) area. The elimination of surface oxygen complexes associated with the as-received carbons upon HT up to 950°C could also result in
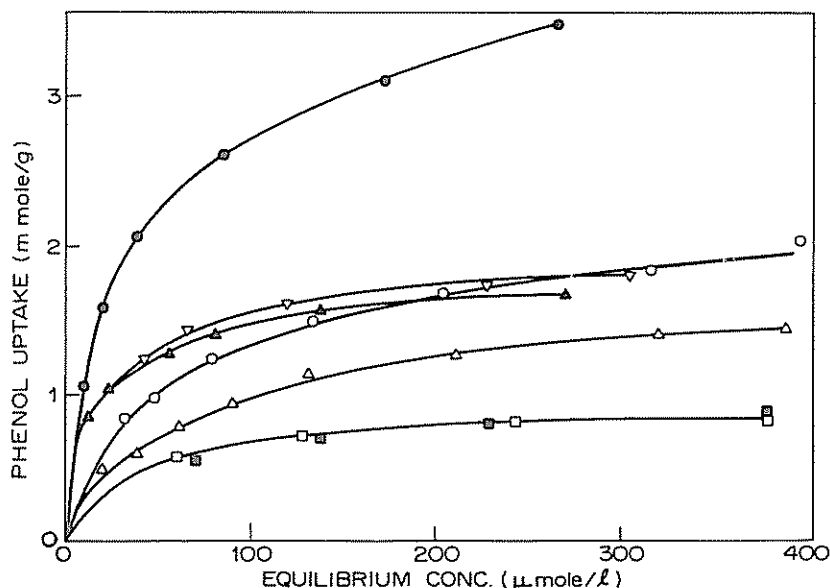
FIG. 8. Phenol adsorption isotherms from aqueous solution on carbons and ion-exchange resins. Carbon A: (△) as-received; (▲) heat treated in N_2 at 950°C; (▽) 950°C heat treated sample subsequently treated with H_2 at 300°C. Carbon F: (○) as-received; (◉) heat treated in N_2 at 950°C. Ion-exchange resins: (□) Ambersorb XE-347; (◼) Ambersorb XE-348.

an increase in phenol uptake in the manner previously discussed. However, the observed increase could also be manifested by another, perhaps simultaneously operating, mechanism. That is, elimination of oxygen complexes increases the pH (that is the degree of alkalinity) of aqueous suspensions of carbons (1). Since phenol is an acidic molecule, its adsorption on a carbon is expected to increase with an increase in the degree of alkalinity of the carbon surface. This could also explain the decrease in phenol uptake following removal of inorganic impurities upon treatment with HCl (Table 2). That is, as-received activated carbons usually contain varying amounts and types of alkali and alkaline earth impurities present initially in the organic precursor used for the production of activated carbon and/or added during the activation step. Their removal, either in part or in total, by acid treatment is expected to decrease the degree of alkalinity of the carbon surface.

It is obvious that the phenol adsorption capacity of commercial activated carbons can be increased by their HT in N_2 at 950°C. However, upon subsequent exposure to air even at ambient temperature the heat-

treated carbons can chemisorb oxygen, resulting in the formation of oxygen complexes which may have an adverse effect on phenol uptake. In order to examine this aspect, as-received and acid-treated Carbon A samples following HT in N_2 at 950°C were stored for 4 weeks in dry air in a desiccator (over Drierite) as well as in "moist" atmospheric air (relative humidity was not monitored). Exposure to dry air has no noticeable effect on phenol uptake for both the samples (Fig. 9). However, in each case exposure to moist air decreases phenol uptake. Exposure of carbons to dry air is expected to result in the formation of predominantly CO-evolving complex(es) (23). Furthermore, the formation of acidic surface complexes is more pronounced in moist air than in a dry atmosphere (2). If the views of Mattson et al. are correct, then the formation of CO-evolving complex (predominantly carbonyl groups) on the carbon surface exposed to dry air should have enhanced phenol uptake. However, such is not seen to be the case in the present study. The decrease in phenol uptake upon exposure to moist air is consistent with the acidic complexes being more effective than the nonacidic complexes in enhancing moisture sorption capacity and in decreasing the pH of the aqueous suspensions (1).

Carbon A following HT in N_2 at 950°C was cooled in N_2 down to 300°C, at which stage N_2 was replaced by H_2. Treatment with H_2 was carried out for 6 h after which the sample was cooled down to room temperature. Following these treatments the carbon adsorbs somewhat more phenol than the sample heat treated in N_2 at 950°C (Fig. 8). Treatment of carbon
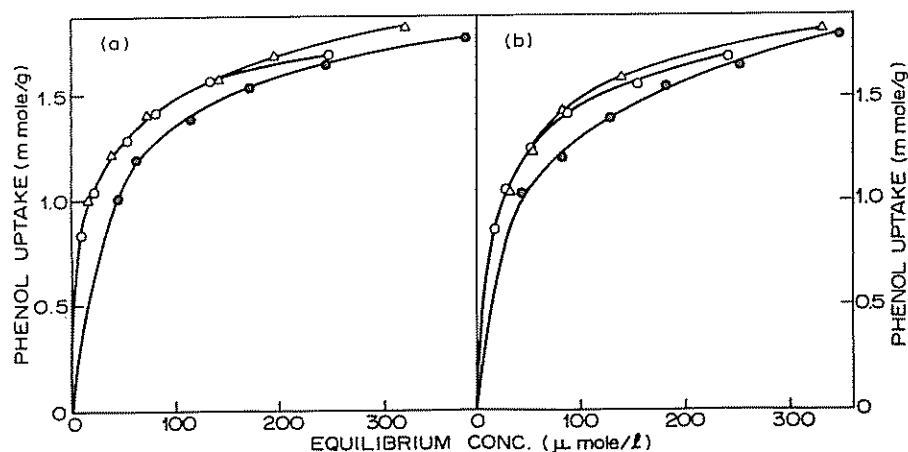

Fig. 9. Effect of exposure of as-received and acid-treated carbon A heat treated in N_2 to dry and moist air on phenol uptake from aqueous solution. Figure 9(a), as-received. Figure 9(b), acid-treated: (○) heat treated in N_2; (△) exposed to dry air; (◉) exposed to moist air.

with H_2 at 300°C is expected to cause little or no hydrogasification. Rather, the predominant step is expected to be the dissociative chemisorption of hydrogen at the "active" carbon sites. Since hydrogen is chemisorbed essentially at the same active sites which are involved in the chemisorption of oxygen (24), it is reasonable to assume that subsequent exposure of the hydrogen-treated carbon to air will minimize chemisorption of oxygen and, hence, decrease phenol uptake. Results of the present investigation thus suggest that phenol uptake capacity of commercial activated carbons can be maximized by heating them in N_2 up to 950°C followed by treatment with H_2 at 300°C.

Treatment of carbons with ammonia at high temperatures results in the formation of C–N surface complexes (1). The nature of these complexes and the manner in which they affect surface behavior and surface characteristics are much less understood than those of the carbon–oxygen complexes. In order to see if the C–N complexes affect phenol uptake, as-received Carbon A was heated with ammonia at 500, 700, and 950°C. The nitrogen contents as well as the CO_2 and N_2 areas of the treated samples are listed in Table 5. Treatment with ammonia at each temperature results in the fixation of significant amounts of nitrogen; the amount fixed is a maximum at 500°C. The formation of C–N complexes has little or no effect on the CO_2 area, but the N_2 area increases significantly. Phenol uptake increases significantly when as-received Carbon A is treated with ammonia at 500°C (Fig. 10). Despite a decrease in nitrogen content of the carbon as HT with ammonia is increased from 500 to 900°C, phenol adsorption capacity continues to increase. However, phenol capacity for the sample treated in ammonia at 900°C is no higher than that for the as-received carbon heated in N_2 at 950°C. On the basis of these limited results, treatment of activated carbons in ammonia does not appear to have advantages insofar as enhancing phenol uptake is concerned.

Ion-exchange resins are being considered at this time as potential

TABLE 5

Properties of Carbon A Treated with Ammonia

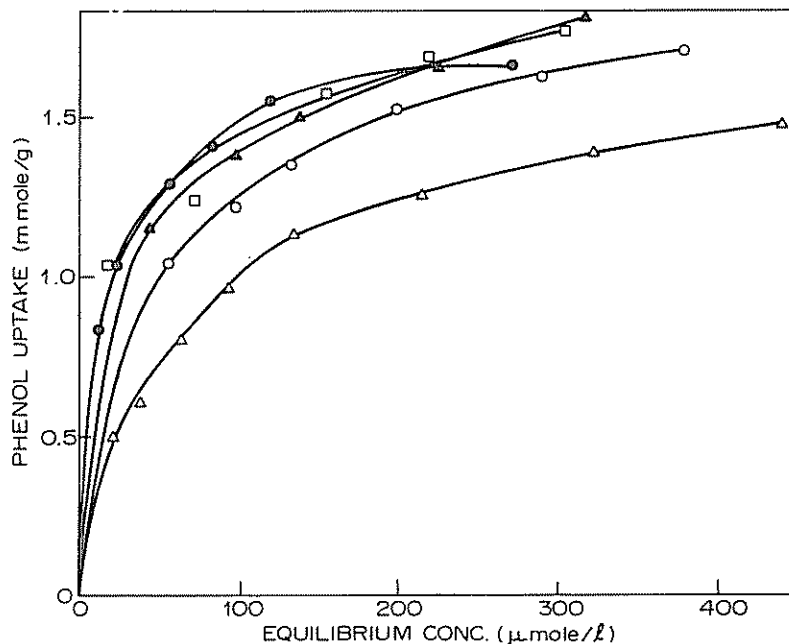| Sample	Surface area (m²/g)		N content (wt-%)
	CO_2	N_2	
As-received	836	975	0.17
Heat treated in N_2 at 950°C	1014	1029	—
Treated with ammonia at (°C):			
500	850	1143	0.64
700	870	1189	0.55
900	850	1133	0.46

FIG. 10. Phenol adsorption isotherms on as-received and NH₃ treated Carbon
A samples: ($\triangle$) as received; ($\circledcirc$) as-received heat treated in N_2 at 950°C. As-
received treated with NH_3: ($\bigcirc$) 500°C; ($\blacktriangle$) 700°C; ($\square$) 900°C.

adsorbents for the removal of organic pollutants from water. In order to
assess their comparative phenol adsorption capacities, two resins,
Ambersorb XE-347 and Ambersorb XE-348, were used in the present
study. Their surface areas are listed in Table 1 and phenol adsorption
isotherms are plotted in Fig. 8. At a given concentration, the resins are
less effective in removing phenol than the activated carbons. Activated
Carbon F, heat treated in N_2 at 950°C, adsorbs roughly four times as
much phenol as the resins at an equilibrium concentration of 100 μmol/L.
These results suggest that activated carbons will continue to be preferred
adsorbents for phenol and possibly other organic pollutants.

Acknowledgment

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