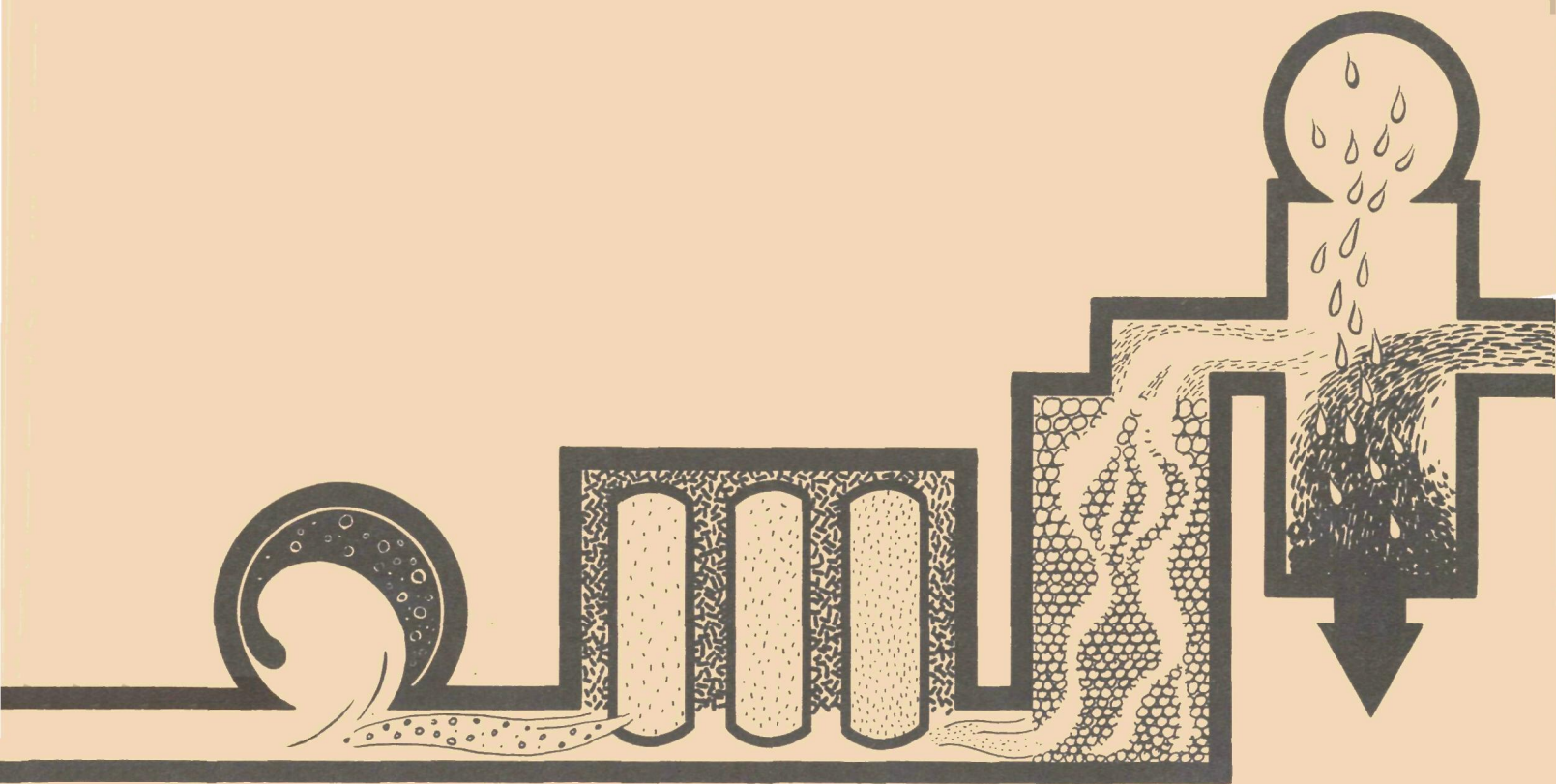




EFFECT OF SURFACE GROUPS ON ADSORPTION OF POLLUTANTS



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EFFECT OF SURFACE GROUPS ON ADSORPTION OF POLLUTANTS

by

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for the

WATER QUALITY OFFICE
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ABSTRACT

It has been shown by experiment that acidic surface oxides on active carbon can profoundly influence the sorption of various pollutant-type molecules from aqueous solution. Not only is the equilibrium sorption capacity of the carbon affected but the rate of sorption is also changed. However, these changes are reversible, for removal of the acidic surface oxides can restore the carbon to its original sorption capacity or beyond. In the cases of sorption of phenol, nitrobenzene, sodium benzenesulfonate and dextrose, surface oxides reduced the sorption capacity of the carbon as well as the speed of sorption. In the case of urea sorption the sorption capacity of the carbon was increased by the presence of acidic surface oxides. It appears that the influence of these surface oxides depends on the relative strength of their interactions with both the water solvent and the solute to be adsorbed.

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SECTION I

INTRODUCTION

Tertiary treatment of secondary sewage effluent is a process that will assume ever greater importance as population and water use continue to grow. The aim of this kind of treatment is to remove from water not only those impurities which can be removed by ordinary biological treatment, but also to remove other organic substances which are oxidized only with difficulty and are, therefore, frequently called refractory or perdurable pollutants. Of the numerous processes which have been considered and evaluated for tertiary treatment of wastewater, adsorption onto active carbon has emerged as one of the most efficient for removing organic impurities and one of the most promising from the standpoint of cost.

Some of the organic compounds that can be removed from water in this way are phenols, cresols, alkylbenzenesulfonates, nitrochlorobenzenes, chlorinated paraffins, butadiene, synthetic dyes, insecticides, fungicides, etc. At present, active carbon is one of the most promising solid adsorbents for this purpose, owing to its commercial availability, high adsorptive capacity, and affinity for a broad spectrum of chemical compounds.

Important tertiary treatment plants are in operation (12,13) at Lake Tahoe and at Pomona, California. The Lake Tahoe plant prevents undesirable nutrients and impurities from reaching the lake by removing most of the phosphate and much of the organic material from secondary sewage effluent. In this plant the secondary effluent from an activated sludge process is chemically coagulated and filtered before treatment with active carbon. The Pomona plant treats effluent directly from an activated sludge process, with no intermediate coagulation or settling step. Here less effective reclamation is achieved, but at far lower expense. A related plant in operation (11) at Nitro, West Virginia, treats river water with active carbon to purify it for domestic use.

In each of these plants saturated or spent carbon, that through use has become ineffective for adsorbing additional impurities, is regenerated by using direct fired furnaces. This regeneration is a three-step process in which the carbon is dried, baked, and activated. After removal of water in the drying step, the second step, baking, carbonizes the organic adsorbate on the surface of the carbon and contained within its porous structure. Baking takes place within a temperature range of 212° to about 1,500°F., and presumably it is accompanied by evolution of gaseous decomposition products and formation of free carbon residue within the pores of the active carbon. The final step, activation, is accomplished by contacting the carbon directly with flue gas which contains additional steam in variable quantity. Activation takes place above about 1,500°F., and during this process the material is oxidized to re-develop a porous structure of large surface area from the spent, baked carbon in which the pore system contains solid decomposition products from the carbonization reaction.

SHORTCOMINGS OF REGENERATION

As might be intuitively expected, this regeneration process does not restore spent, active carbon to its original adsorptive capacity. This shortcoming occurs in addition to actual loss of carbon resulting from burn-off, mechanical attrition, and other purely physical losses. Thus, after regeneration, the carbon does not possess the original specific adsorptive capacity, and this may be ascribed to possibly diminished specific surface area, possible alterations in the pore structure of the carbon adsorbent, and possible chemical change in the nature of the adsorbing surface. Presumably, all three of these phenomena play a role in altering the adsorptive capacity of regenerated, active carbon. To date no quantitative assessment exists as to the relative contributions from changes in pore structure, specific surface area, and surface chemistry in bringing about this reduction of adsorptive capacity.

It is clear that lowering the specific surface area and narrowing the pores of a carbon adsorbent tend to reduce its adsorptive capacity, but the influence on adsorption of chemical alteration of the carbon surface is somewhat more remote from intuitive understanding. The purpose of the work reported below is to shed more light on the possible importance of the nature of the carbon surface in adsorption, as distinct from the influence of pore structure and specific surface area.

SURFACE CHEMISTRY OF CARBON ADSORBENTS

Active carbon is one form of black, microcrystalline (sometimes called amorphous) carbon. Its underlying structure is fundamentally graphitic, as was shown by Hofmann and Wilm (1) using X-ray diffraction. A visualization of this structure consists of packets of graphite-like layer planes of some three to thirty layers about 10 to 100 Å thick. A graphitic layer, which may be regarded as analogous to a very large, polynuclear aromatic molecule, contains carbon atoms joined by σ bonds to three neighboring carbon atoms with the fourth electron of each atom participating in a π bond (sp^2 hybridization). In graphite, the resulting layers are stacked with a separation of about 3.35 Å in the sequence ABAB, although some ABCABC sequence may also occur (2). In microcrystalline carbon, the interlayer spacing is larger than in graphite, that is, about 3.6 Å, and the stacking sequence is greatly perturbed with the result that many graphitic layer planes are tilted with respect to one another. The layers of both graphite and microcrystalline carbon are held together relatively weakly by van der Waals forces. In addition, there may be present in microcrystalline carbon a considerable content of disorganized tetrahedrally bonded carbon (3,4) often crosslinking different layers. Moreover, foreign atoms are always present in differing amounts, and they may be bound at the edges of the crystallites to form functional groups or incorporated within the graphitic layers to form heterocyclic ring systems.

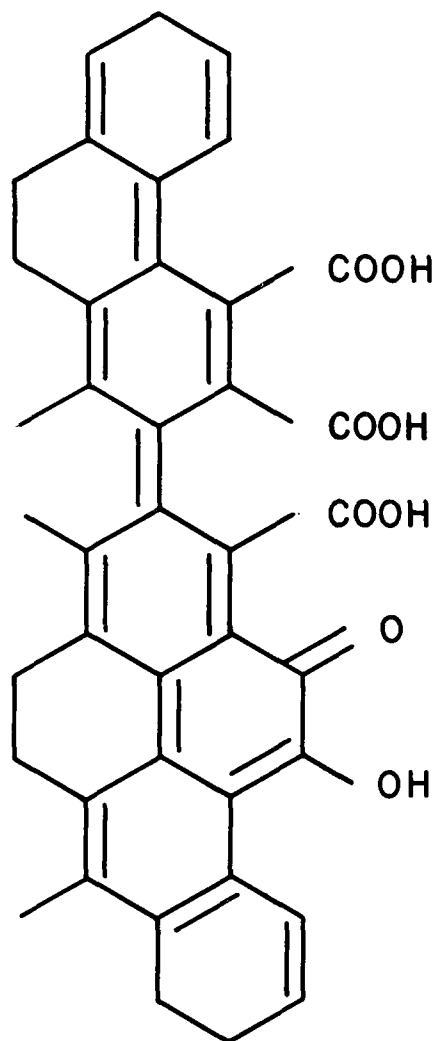
Because free valences at the edges of the graphitic layer planes of microcrystalline carbon are very reactive and form compounds with any suitable foreign atoms present, functional groups or surface compounds can be expected almost exclusively at the layer edges. Foreign atoms or molecules can be only weakly adsorbed on the basal faces by means of the graphitic π electron system, except where they are bound at lattice defects. Most important and best known among the surface compounds of carbon are those with oxygen and sulfur, although other elements, such as chlorine and hydrogen, can also combine with elemental carbon. Of these compounds the surface oxides of carbon have received the most study, and the role of these oxides in adsorption is the principal topic of this report. In particular, the concern here is the acidic surface oxides of carbon, which are formed under the most usual conditions of treatment and manufacture of microcrystalline carbon products like active carbon. Basic surface oxides also occur, but less frequently, and their nature and structure

have not yet been elucidated very thoroughly. Garten, Weiss, et al. (5) claim that basic oxides are produced during oxidation at high temperatures, but Boehm (6) has pointed out that they are formed after an outgassed carbon surface comes into contact with oxygen after cooling in an inert atmosphere.

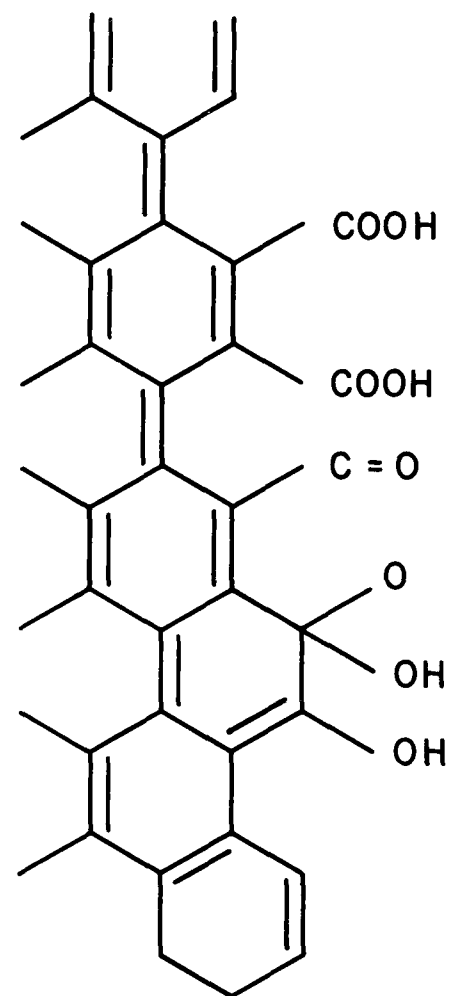
Of the many techniques for characterizing the acidic surface oxides of carbon, the method used extensively by Boehm, Diehl, et al. (7) has been employed in the present work. In an extension of earlier work (5,8), these investigators used typical identification reactions of organic chemistry to characterize oxygen chemisorbed on carbon as comprising four different types of acidic surface groups: a strongly acidic carboxyl group, a more weakly acidic carboxyl group, a phenolic hydroxyl group, and a carbonyl group. Figure 1 shows a schematic structure representation of these groups in which the difference between the two kinds of carboxyl groups is related to their ability to form a lactone or lactol. These acidic functional groups can be identified by their reaction (or failure to react) with bases of different strength. Thus, group I is neutralized by each of the bases sodium bicarbonate, sodium carbonate, and sodium ethoxide; group II is neutralized by sodium carbonate or stronger bases but not by sodium bicarbonate, etc. Accordingly, simple titration with different bases serves to identify the acidic surface oxides present on a given sample of carbon.

These acidic functional groups can be produced by oxidation in air or pure oxygen or by mixing the carbon sample with aqueous solutions of oxidizing agents like sodium hypochlorite, potassium permanganate, or ammonium persulfate. It is also possible to remove partially the acidic functional groups by reduction or vacuum out-gassing at elevated temperatures. In addition, these groups can be made to react in other ways like esterification, formation of acid chlorides, acetylation, etc.

It was the purpose of the work reported here to attempt to learn more about how the nature of the carbon surface influences adsorption of typical organic compounds from aqueous solutions. In particular, because acidic surface oxides are commonly present on most commercial carbons and because they are rather easy to form on as well as remove from the surface of carbon, the present work focused on these groups and upon their influence on the adsorption process. In this work, the adsorptive capacity and the rate of adsorption for different carbons treated in different ways were observed for several different adsorbates of importance for tertiary waste treatment.



OPEN FORM



LACTONE FORM

FIGURE 1 POSSIBLE STRUCTURES OF CARBON SURFACE OXIDES

SECTION II

SUMMARY AND CONCLUSIONS

It has been shown by experiment that acidic surface oxides on active carbon can profoundly influence the sorption of various pollutant-type molecules from aqueous solution. Not only is the equilibrium sorption capacity of the carbon affected but the rate of sorption is also changed. However, these changes are reversible, for removal of the acidic surface oxides can restore the carbon to its original sorption capacity or beyond. In the cases of sorption of phenol, nitrobenzene, sodium benzenesulfonate and dextrose, surface oxides reduced the sorption capacity of the carbon as well as the speed of sorption. In the case of urea sorption, the sorption capacity of the carbon was increased by the presence of acidic surface oxides. It appears that the influence of these surface oxides depends on the relative strength of their interactions with both the water solvent and the solute to be adsorbed.

SECTION III

RECOMMENDATIONS

Further experimental and theoretical work is needed to elucidate the mechanism by which surface functional groups on adsorbents influence the adsorption of various substances from aqueous solution. Hopefully, such work may ultimately lead to the knowledge required to predict by theory the behavior that is now accessible only by experiment.

SECTION IV

EXPERIMENTAL PHASE

The carbon adsorbents used in this project were: Union Carbide's Columbia Carbon LC325 and NXC 12/28X, Atlas Chemical's Darco S51, Calgon's Filtrasorb 300W, and Cabot Corporation's Black Pearls 607. The adsorbates used in this project were: sodium benzenesulfonate, phenol, nitrobenzene, dextrose, and urea; these represent respectively a detergent, two "refractory" organic compounds, a sugar commonly present in secondary municipal sewage effluent and a molecule of relatively large dipole moment.

Chemical analysis of aqueous adsorbate solutions was performed using ultraviolet spectrophotometry at 270.0 m μ for phenol, at 216.0 m μ for sodium benzenesulfonate, and at 267.8 m μ for nitrobenzene. It was necessary to use differential refractometry for solutions containing large concentrations of phenol. A standard spectrophotometric technique (9) was employed for determining urea. Concentrations of dextrose were determined by measuring the optical rotation of plane polarized light passed through the solutions, using a polarimeter.

Acidic oxide functional groups were formed on the carbon surfaces by room temperature oxidation in aqueous solutions of ammonium persulfate. These surface oxides were removed from the carbon by exposure to hydrogen gas produced by the action of HCl on Zn amalgam, or by heating the carbon samples to temperatures up to 890°C in vacuo. The nature and concentrations of surface oxides on the carbon surfaces were determined by titrating the samples using bases of different strength using the technique of Boehm (7). Specific surface areas of the carbon adsorbents were determined by the standard BET technique (10) using nitrogen as the adsorbate. Specific surface areas and base consumption for the carbon samples are recorded in Table 1.

Adsorption experiments were carried out by equilibrating samples of carbon adsorbent with the various analyzed solutions of adsorbate for periods up to several hours. These mixtures were stirred or shaken during the exposure. After equilibration, the carbon was filtered from the solution which was then re-analyzed. Kinetic experiments were performed by adding carbon of known, large particle size to a well-stirred vessel of adsorbate solution; periodically, stirring was stopped and, after the carbon particles had settled, a sample of clear solution was withdrawn for chemi-

Table 1

SPECIFIC SURFACE AREA AND BASE CONSUMPTION FOR SEVERAL CARBONS

Carbon Sample Identification*	BET(N ₂) Area m ² /gm	Base Consumption Meq/gm			
		NaOEt(tot.acidity)	NaOH	Na ₂ CO ₂	NaHCO ₃
LC325	1200	0.38	0.12	0.11	0.11
LC325 O	556	4.15	4.22	3.10	2.20
LC325 OR	40	1.87	1.92	2.04	0.84
P607	665	2.40	1.88	1.34	0.85
P607 O	668	3.06	2.25	1.69	0.97
P607 R	663	1.86	1.31	0.97	0.48
P607 OR	5.3	2.42	1.94	1.42	0.88
P607 OROROR	562	1.56	1.26	0.90	0.80
S51	586	1.08	0.71	0.48	0.40
S51 O	596	4.21	3.57	2.45	1.85
S51 OR	836	2.15	1.81	1.12	0.80
S51 OD	725	0.60	0.60	0.25	0.20
LC325 -T	1076	0.59	0.48	0.28	0.30
LC325 O -T	861	3.10	2.92	2.05	1.50
LC325 OR -T	840	2.46	2.10	1.29	0.92
CF300	950	0.70			
CF300 O		3.50			
NXC		0.65	0.35	0.07	0.04
NXC O		3.72	4.47	3.24	2.32

*The suffix O means oxidized, R means reduced, D means outgassed at 890°C under vacuum, OR means oxidation followed by reduction, etc.

No suffix means the carbon sample was simply wasted with no further treatment. The suffix -T has been used to distinguish one set of LC325 samples from another set.

cal analysis. In the case of dextrose adsorption, it was found that the entire experiment could be carried out in the polarimeter cell. All adsorption experiments were carried out at constant temperature. For kinetic experiments a narrow size range of carbon particles was employed in each case - this narrow size range was obtained by sieving through U. S. Standard sieves.

More detailed descriptions of analytical procedures and techniques may be found in the various reports and publications which resulted from this project and which are listed in Section 7.

SECTION V

DISCUSSION

The influence of surface oxides on sorption of phenol from aqueous solution is clearly shown by the adsorption isotherms plotted in Figure 2. The uppermost isotherm in this Figure represents the adsorption of phenol on acid-washed but otherwise untreated active carbon LC325; the lowest isotherm in this Figure represents adsorption of phenol on carbon oxidized, as outlined in the Experimental Section, on order to produce a large population of surface functional groups or oxides on the carbon surface. The intermediate isotherm is for oxidized carbon that was subsequently reduced with hydrogen before adsorption experiments. These carbons are designated "O" for oxidized and "OR" for oxidized followed by reduction; no such designation indicates that the carbon was merely washed. Figure 3 shows the same kind of behavior for the adsorption of nitrobenzene on the same carbons as for Figure 2.

Figures 2 and 3 show that oxidation of the carbon sorbent lowers considerably its adsorption capacity for phenol and nitrobenzene on a "per gram of carbon" basis. Quite similar behavior is also observed if the isotherms are plotted on the basis of amount adsorbed per unit BET specific surface area of the carbon. It is clear that reduction of the oxidized carbon surface using hydrogen partially restores its adsorption capacity for phenol and probably also for nitrobenzene. Figure 4 shows the influence of surface acidity on sorption capacity expressed as percentage of BET surface area occupied by phenol (assuming the phenol molecule lies flat on the carbon surface) at concentrations corresponding to the plateau of isotherms similar to those of Figures 2 and 3; here percentage of area occupied is plotted versus total surface acidity measured as meq of $\text{NaOCH}_2\text{CH}_3$ neutralized per gram of carbon. Data for both the carbon black P607 and active carbon LC325 are included on Figure 4.

Although the data of Figure 4 show that a threefold increase in surface acidity from about 1 meq/gm to 3 meq/gm produces a corresponding threefold decrease (from about 15% to 5%) in the percentage surface area occupied by the adsorbate, it should not be concluded therefrom that the loss in adsorptive capacity results from direct steric interference by surface acidic groups which occupy surface area that would otherwise be available to the adsorbate. On the

FIGURE 2.

ADSORPTION ISOTHERMS OF PHENOL ON ACTIVATED
COLUMBIA CARBON LC325 FROM AQUEOUS SOLUTION
(30°C, ONE WEEK EQUILIBRIUM TIME)

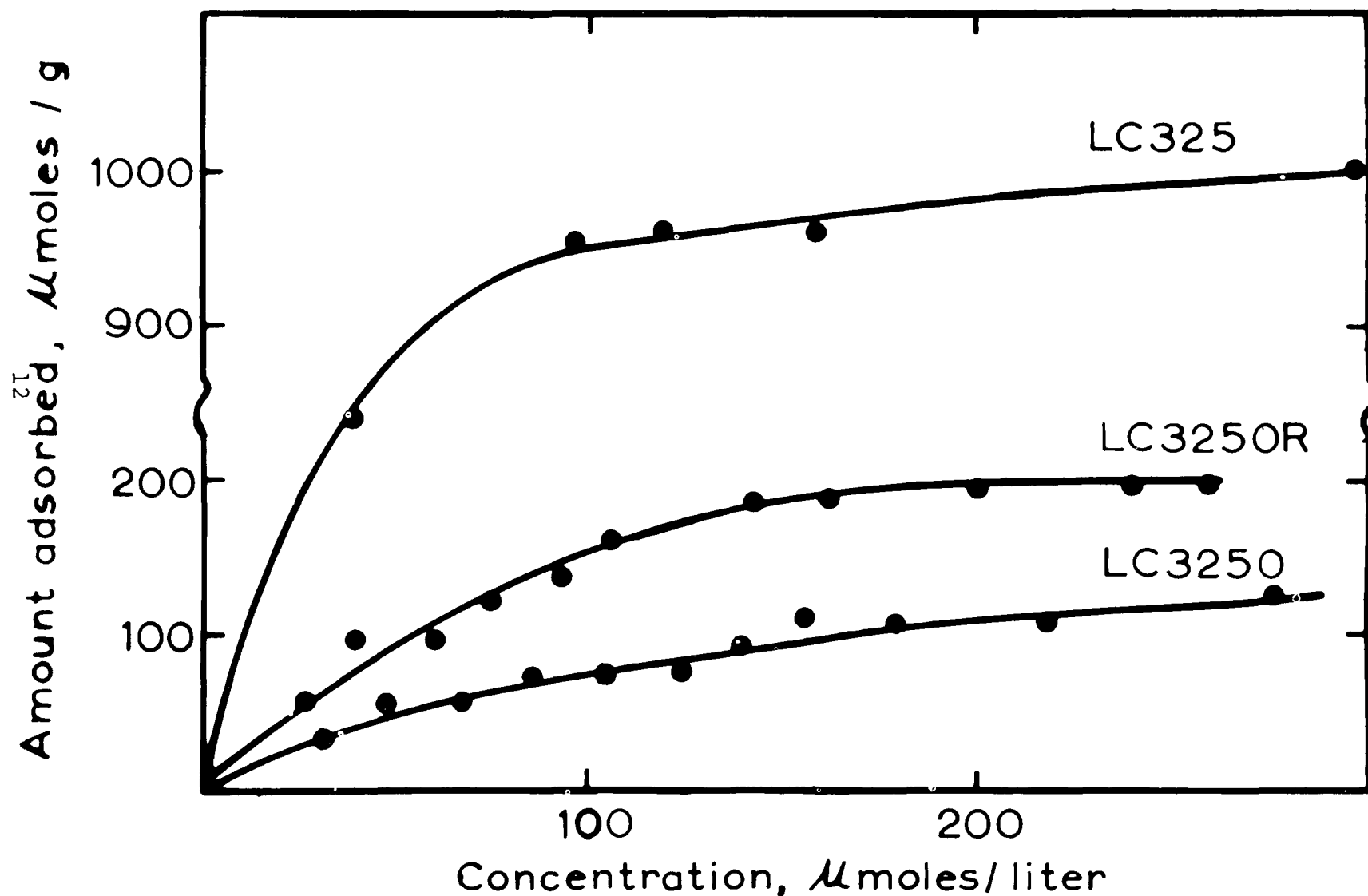
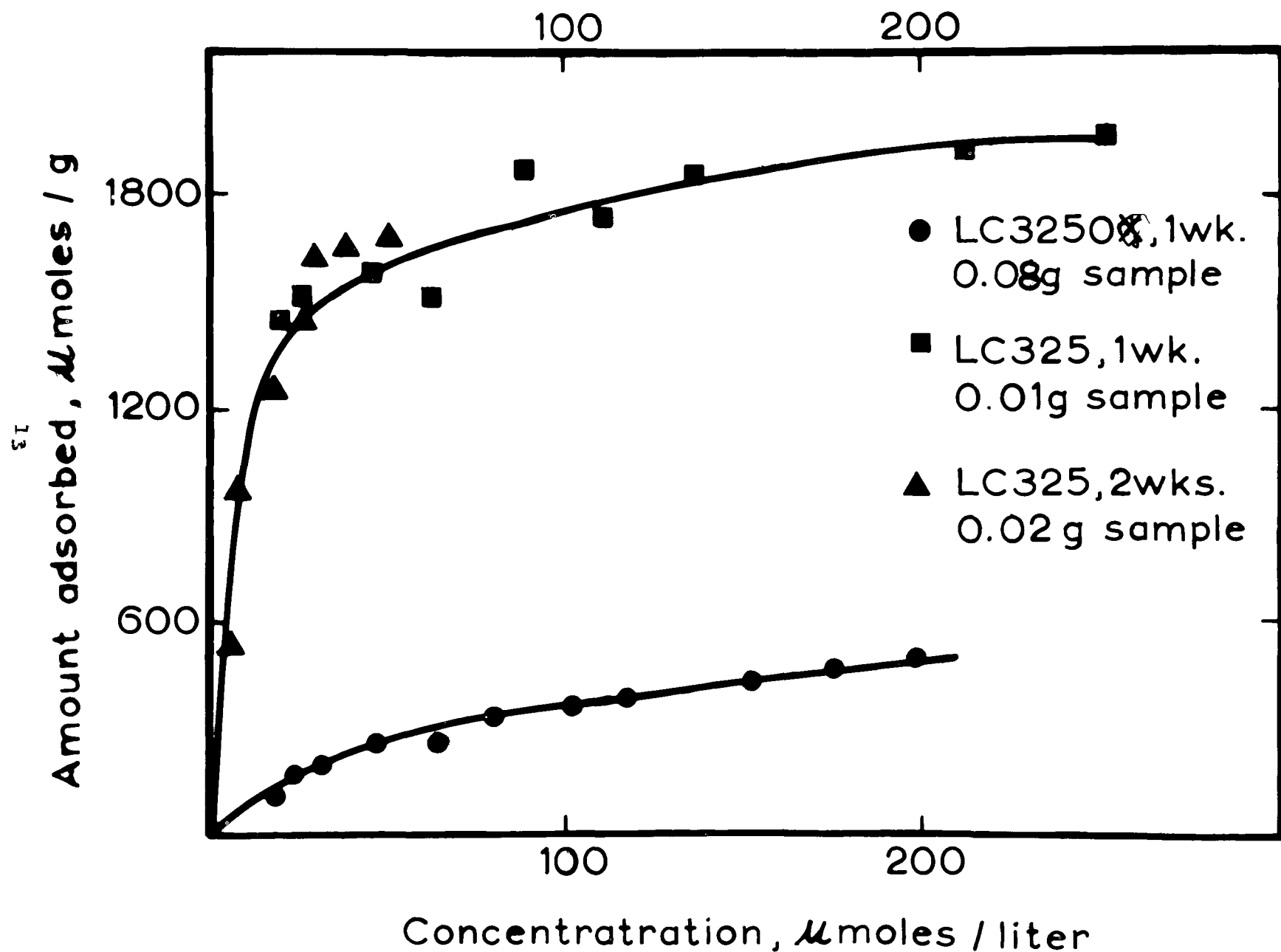


FIGURE 3.

ADSORPTION ISOTHERMS OF NITROBENZENE ON ACTIVATED COLUMBIA CARBON LC325 FROM AQUEOUS SOLUTION, 30° C



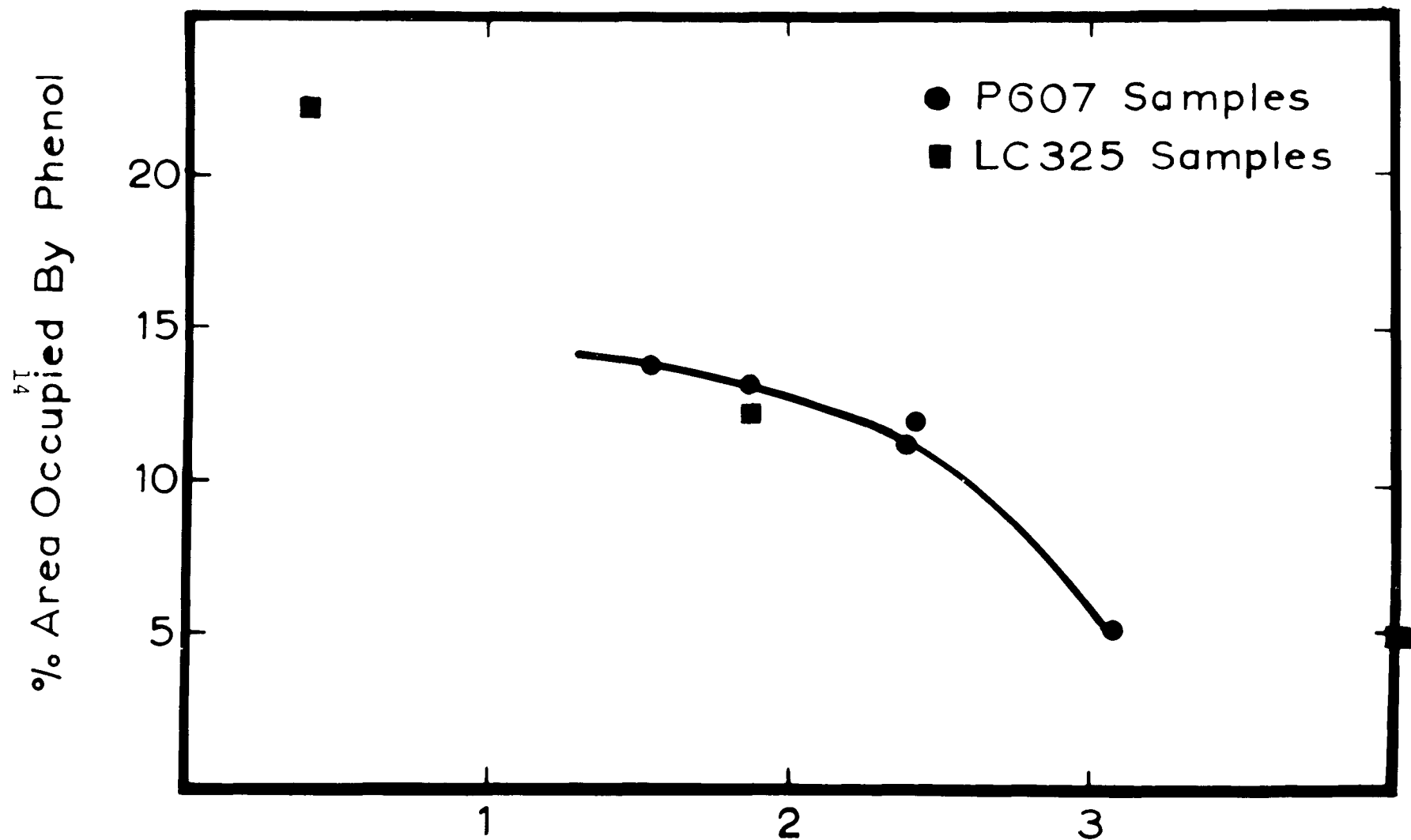


FIGURE 4.

Total Acidity meq / g

% AREA OCCUPIED BY PHENOL VS. TOTAL AMOUNT OF ACIDITY

basis of the model proposed herein for the carbon surface, the acidic groups would be expected to be concentrated at the edges of the hexagonal layer planes, whereas the major portion of surface active for physical adsorption would be located on the flat, basal surfaces - not the edges - of the layer planes. It may be that the acidic surface groups merely block small pores and thereby the surface area within such pores becomes inaccessible. Another explanation could be based on the ability of oxygen to attract electrons from the π -electron system of the layer planes toward the edges of these planes and thereby affect the sorptive properties of the layer planes. It will be seen below that the presence of acidic functional groups actually raises the adsorptive capacity of the layer planes for urea and this fact would tend to support the electronic interpretation. Other interpretations could be advanced based on the relative strength of interaction of the acidic groups with water or phenol on the one hand and with water or urea on the other hand. Unfortunately, neither the chemical nature nor the concentrations of the acidic groups are known with sufficient certainty or accuracy to make a firm interpretation of these results.

Additional isotherms for phenol adsorption appear in Figure 5. However the data in Figure 5 are for a different activated carbon, Darco S51, and isotherms are shown here for the acid washed carbon (S51), oxidized carbon (S51 O), oxidized and reduced carbon (S51 OR) and for oxidized carbon that was subsequently outgassed at high temperature (S51 OD). Note in this Figure that the ranking of adsorption capacity for S51, S51 O and S51 OR is identical to that for LC325, LC325 O and LC325 OR shown in Figures 2 and 3 and discussed above. However, it is clear from Figure 5 that oxidation followed by vacuum outgassing at elevated temperature (S51 OD) produces a carbon of larger adsorption capacity than the starting material (S51). This behavior can be attributed to two differences between S51 and S51 OD: the S51 OD had a larger BET specific surface area and a lower population of acidic surface sites (on either a per gram or per unit surface area basis) than did the untreated S51 active carbon. Note, however, that the isotherm of Figure 5 is expressed on a surface concentration basis (μ moles/m²) and, therefore, the sorption capacity difference between S51 and S51 OD evident from Figure 5 may be attributed to a difference in population of acidic surface sites on the carbon adsorbent.

Figure 6 shows that the adsorption of sodium benzene-sulfonate on active carbon LC321 is affected in the same way by oxidation and reduction as is the adsorption of nitrobenzene and phenol. Figures 7 and 8 show similar behavior

FIGURE 5 ADSORPTION ISOTHERMS OF PHENOL ON ACTIVATED CARBON "DARCO S51"
IN AQUEOUS SOLUTION, 30°C, 3 DAYS EQUILIBRIUM TIME

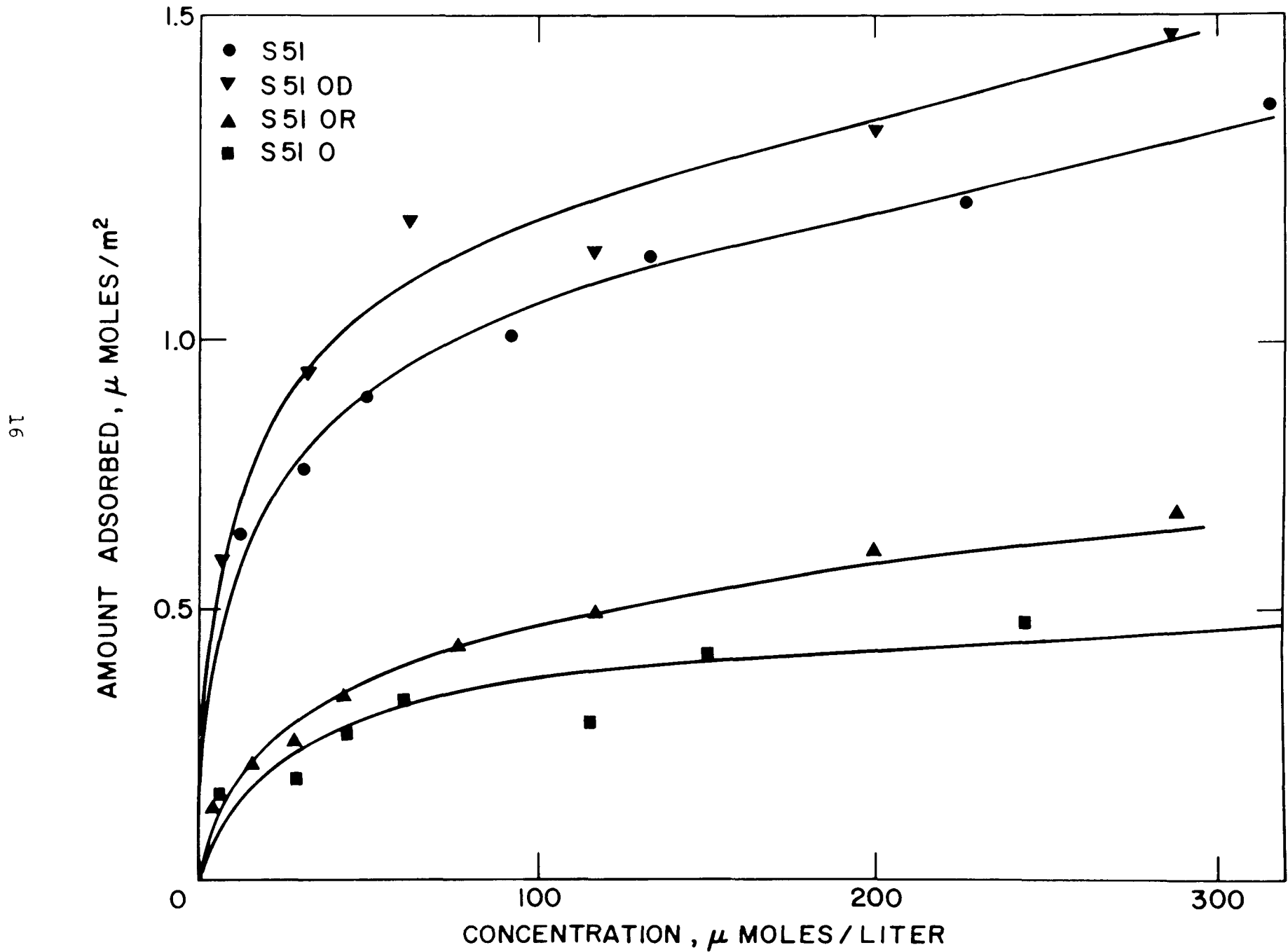


FIGURE 6 ADSORPTION ISOTHERMS OF SODIUM BENZENE SULFONATE ON ACTIVATED CARBON "COLUMBIA LC325" IN AQUEOUS SOLUTION, 30°C, 3 DAYS EQUILIBRIUM TIME

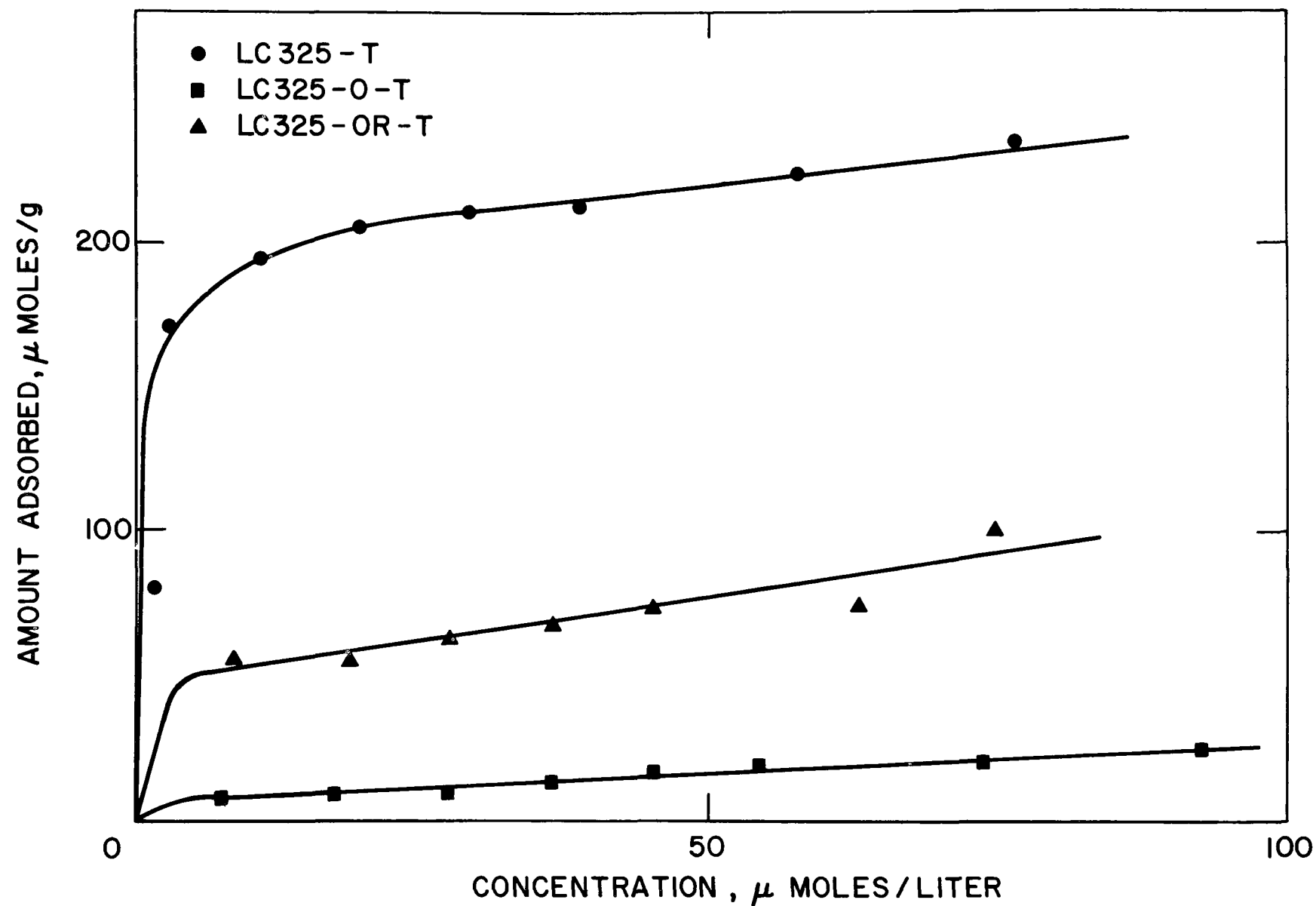


FIGURE 7 ADSORPTION ISOTHERMS OF DEXTROSE ON ACTIVATED CARBON (COLUMBIA LC325)
IN AQUEOUS SOLUTION AT 30.0°C FOR 1.0 HOUR EQUILIBRIUM TIME ON A
PER GRAM BASIS

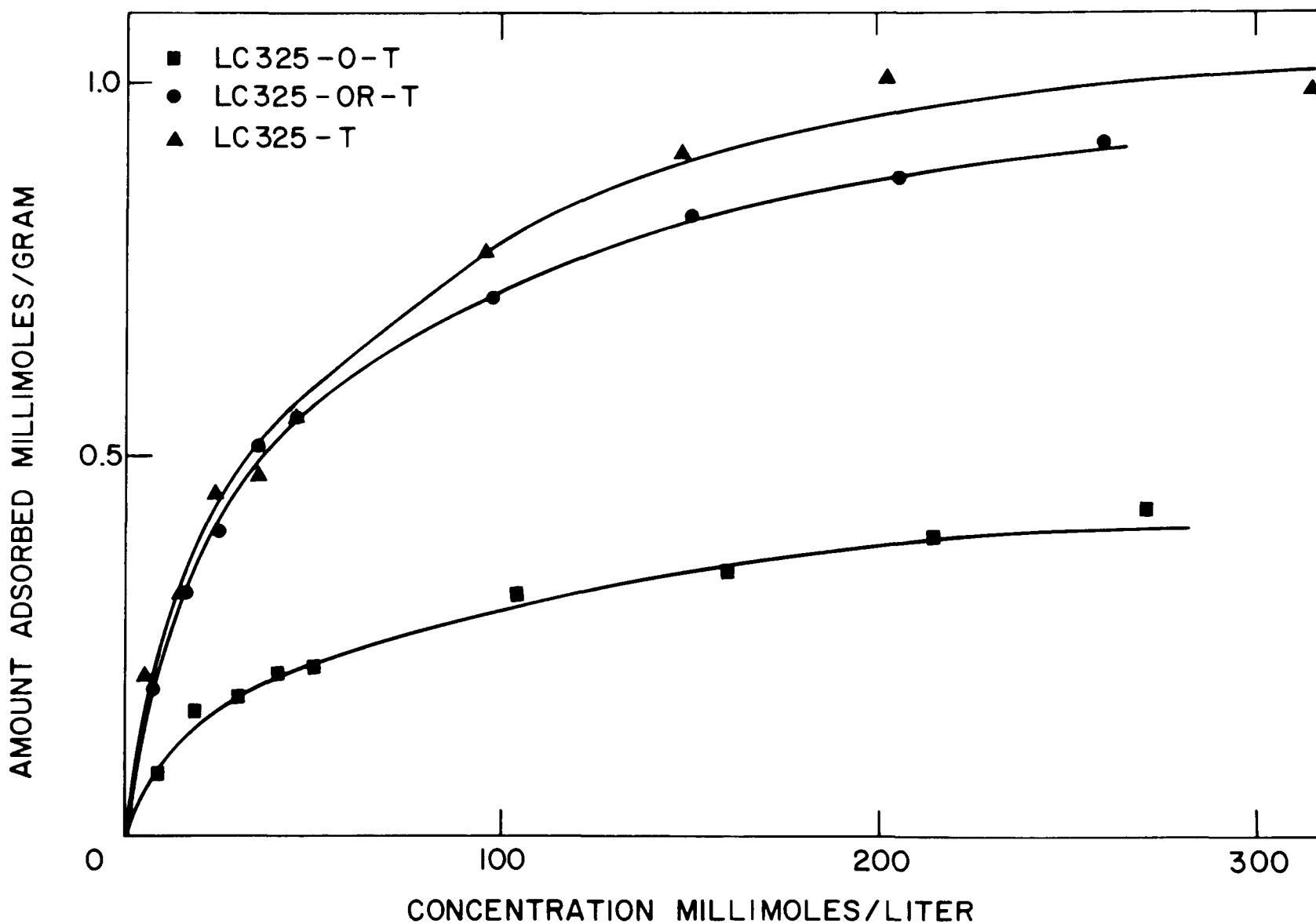
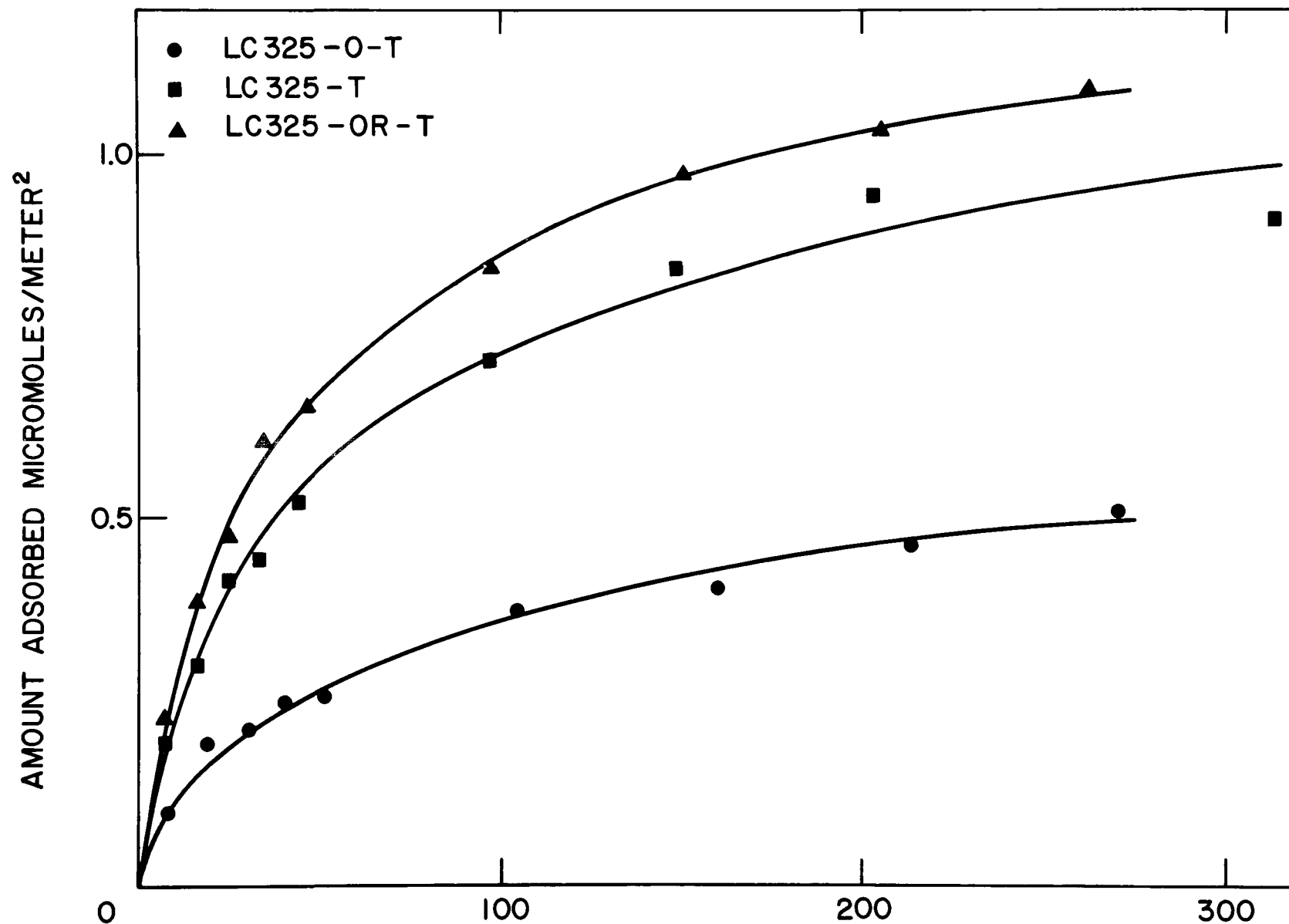


FIGURE 8 ADSORPTION ISOTHERMS OF DEXTROSE ON ACTIVATED CARBON (COLUMBIA LC325)
IN AQUEOUS SOLUTION AT 30.0°C FOR 1.0 HOUR EQUILIBRIUM TIME.
(PER UNIT BET SURFACE AREA BASIS)



for the sorption of dextrose on samples of LC325 treated in the same way. In Figure 7 the adsorption isotherms are plotted on a per-gram basis whereas in Figure 8 the quantities adsorbed are expressed on a per unit BET specific surface area basis.

The adsorption isotherms for urea on LC325 and LC325 O, which appear in Figure 9, show a ranking behavior which is opposite to that for all the other adsorbates discussed above. Oxidizing the carbon surface, therefore, appears to increase its sorption capacity for urea from aqueous solution in contrast to the behavior of phenol, nitrobenzene, sodium benzenesulfonate and dextrose. The reason for this behavior may lie in the relative magnitudes of attractive forces between carbon and water in comparison with the attractive forces between carbon and adsorbate. Based on the expected strength of hydrogen bonding between water and acidic sites on the carbon surface, the water may block part of the carbon surface and interfere with adsorption thereon by phenol, nitrobenzene, sodium benzenesulfonate and dextrose. On the other hand, urea which can also strongly hydrogen bond to surface oxides on carbon may be able to compete with water for these sites more effectively than can the other adsorbates.

The influence of surface oxides on the rate of adsorption of dextrose on carbon is revealed by Figures 10 and 11. In each of these Figures the concentration of dextrose solution is plotted versus the square root of time measured from the introduction of a known amount of carbon into the solution. Figure 10 gives these results for untreated carbon at 19°C and 40°C whereas Figure 11 shows results for oxidized carbon at 40°C. Based on the extremely simple relationship:

$$\text{rate of adsorption} = K t^{\frac{1}{2}}$$

the rate constant K can be evaluated from the slopes of the curves in Figures 10 and 11. At 40°C K for adsorption of dextrose on untreated carbon is 867 μ moles/gm, $\text{hr}^{\frac{1}{2}}$ (Figure 10) whereas K = 476 μ moles/gm, $\text{hr}^{\frac{1}{2}}$ for adsorption of dextrose on oxidized carbon at the same temperature (Figure 11). Further evidence for the inhibiting effect of surface oxides on rate of adsorption appears in Figure 12 where the rate constant K for dextrose adsorption is plotted versus the concentration of oxidizing agent used to treat the carbon.

By plotting the logarithm of the rate constant versus the reciprocal of absolute temperature it is possible to estimate an apparent activation energy. Figure 13 shows these plots for the adsorption of dextrose on CF300 and CF300-W and Figure 14 for the adsorption of phenol on active

FIGURE 9 ADSORPTION ISOTHERM OF UREA ON ACTIVATED CARBON (COLUMBIA LC325)
IN AQUEOUS SOLUTION AT 30.0°C FOR 0.5 HOURS EQUILIBRIUM TIME ON
A PER GRAM BASIS

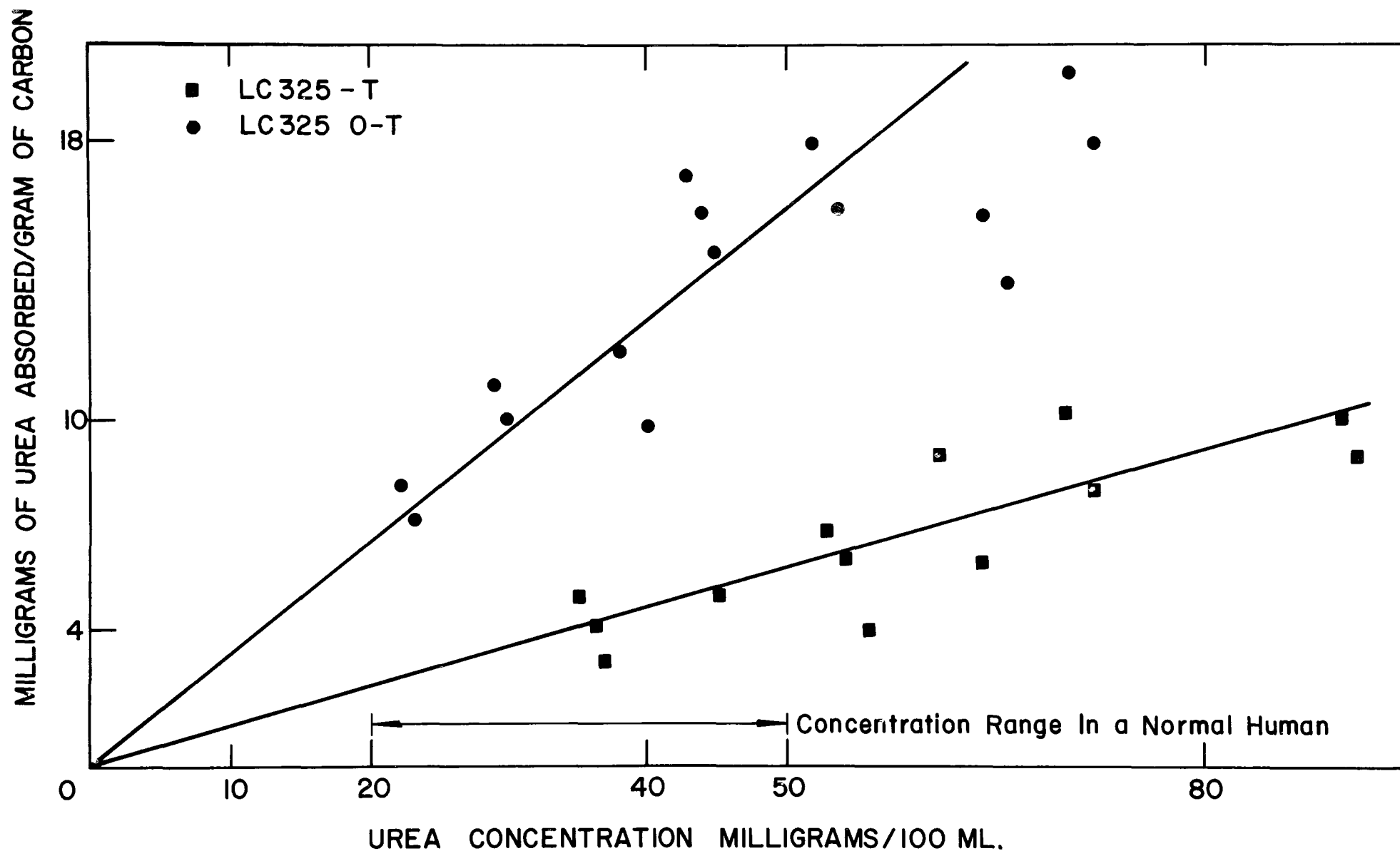


FIGURE 10 RATES OF ADSORPTION OF DEXTROSE ON CF300 W IN AQUEOUS SOLUTION,
PARTICLE SIZE RANGE 2.38-2.83 MM.

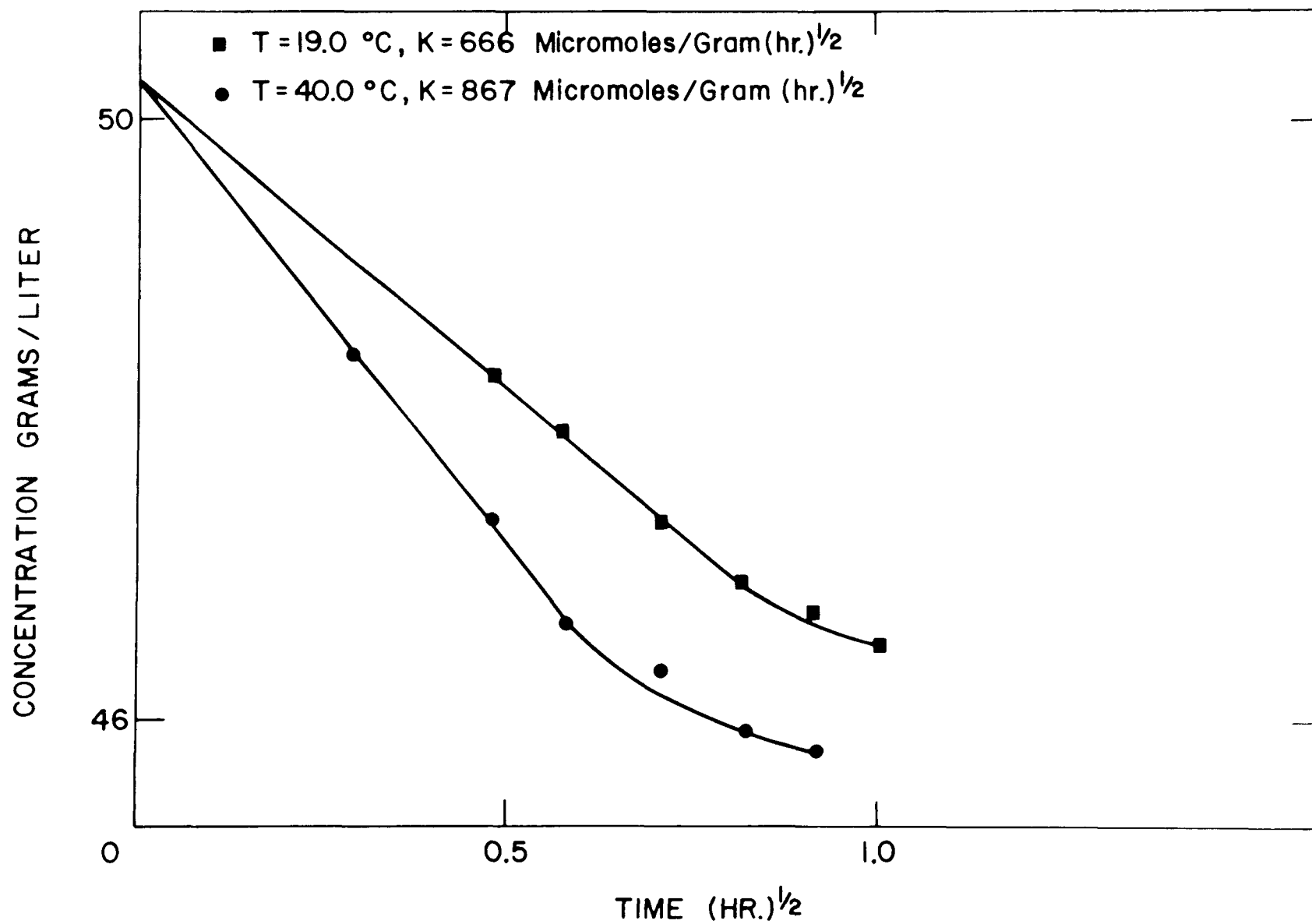


FIGURE 11 RATE OF ADSORPTION OF DEXTROSE ON CF300-0 IN AQUEOUS SOLUTION
AT 40.0°C, PARTICLE SIZE RANGE 2.38-2.83 MM., $(\text{NH}_4)_2\text{S}_2\text{O}_8$ -0.4 MOLAR.

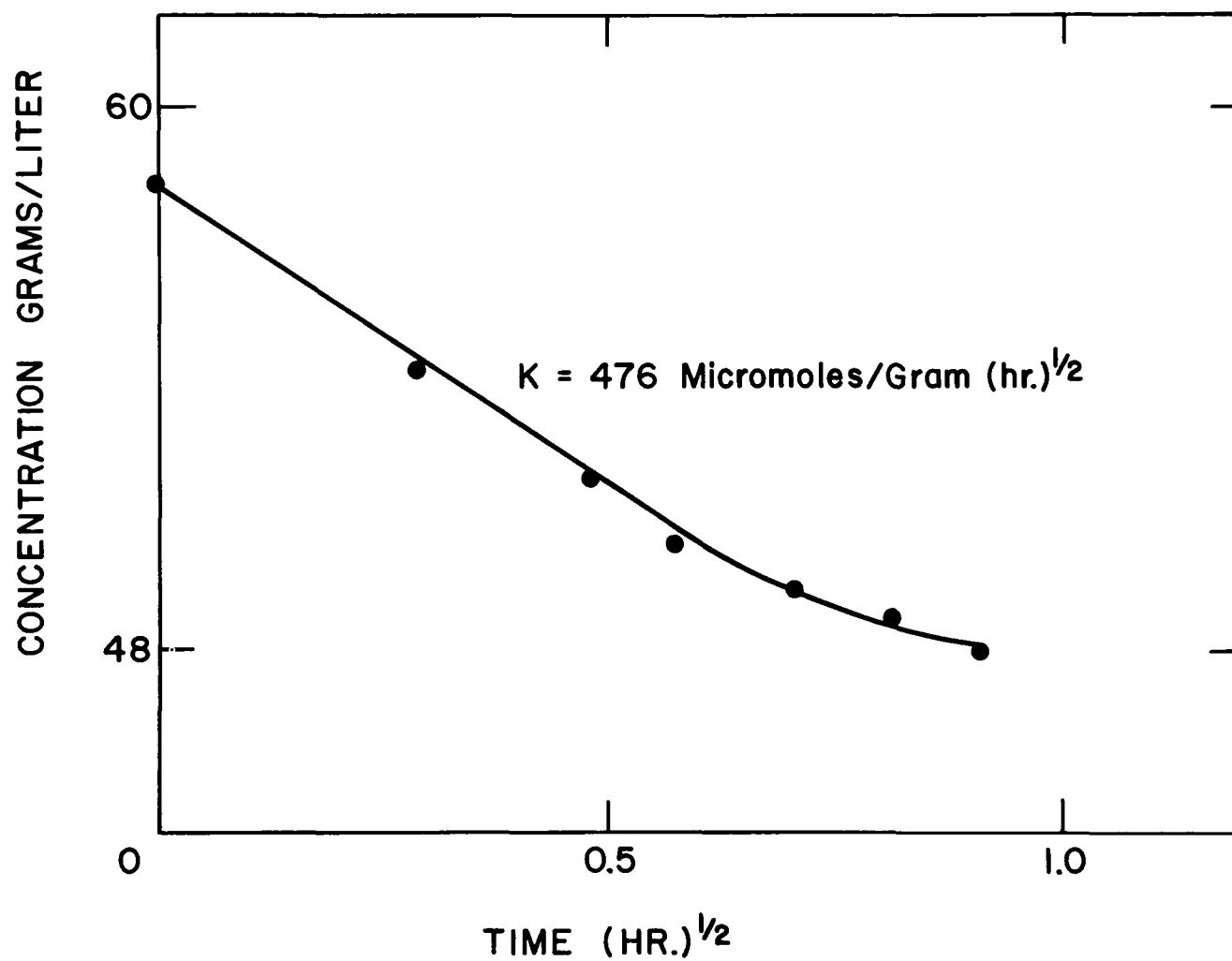


FIGURE 12 EFFECT OF $(\text{NH}_4)_2\text{S}_2\text{O}_8$ CONCENTRATION ON THE RATE CONSTANT K IN AQUEOUS SOLUTION, PARTICLE SIZE RANGE 2.38-2.83 MM., AT 19.0°C CF300 CARBON

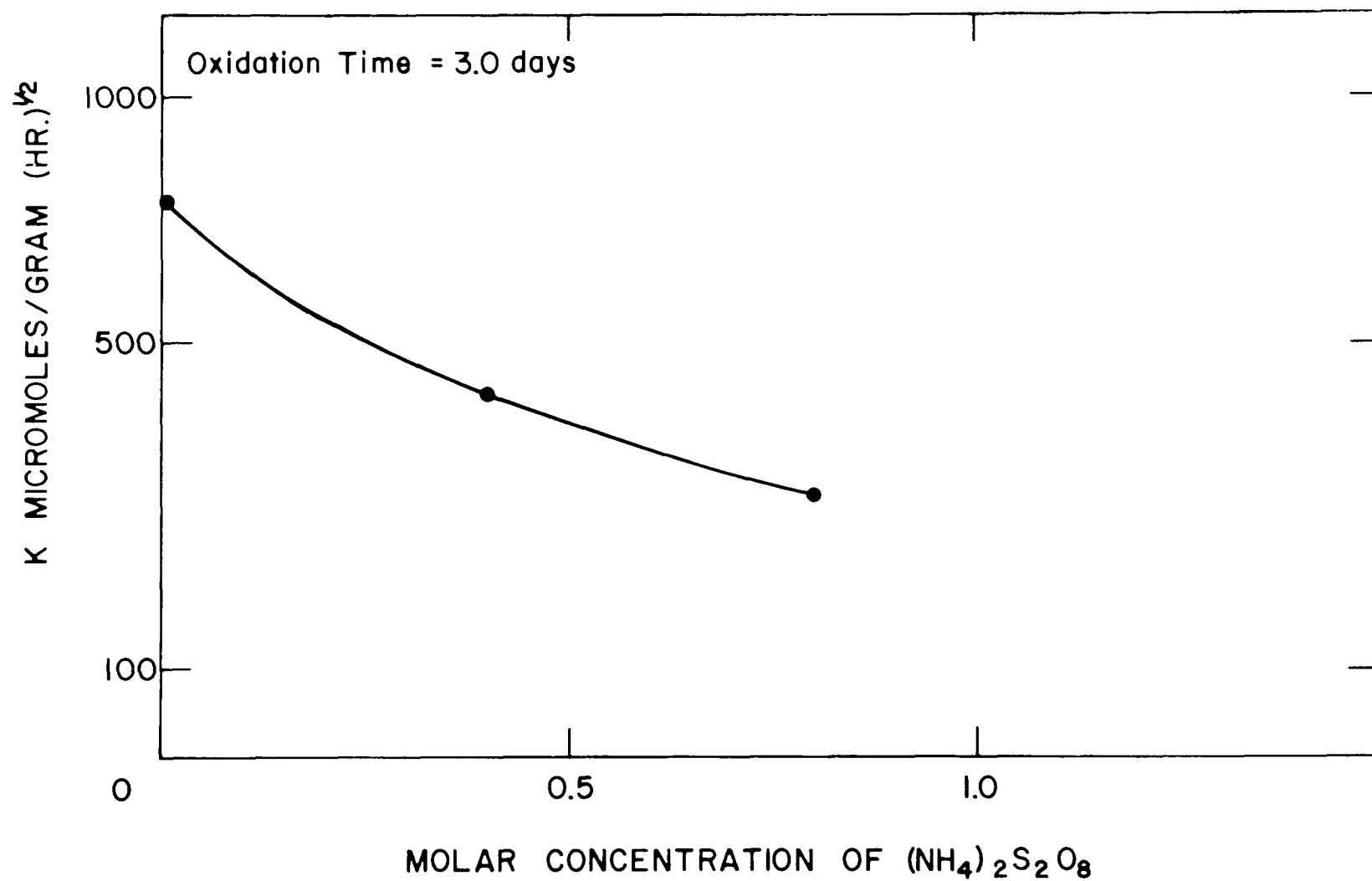
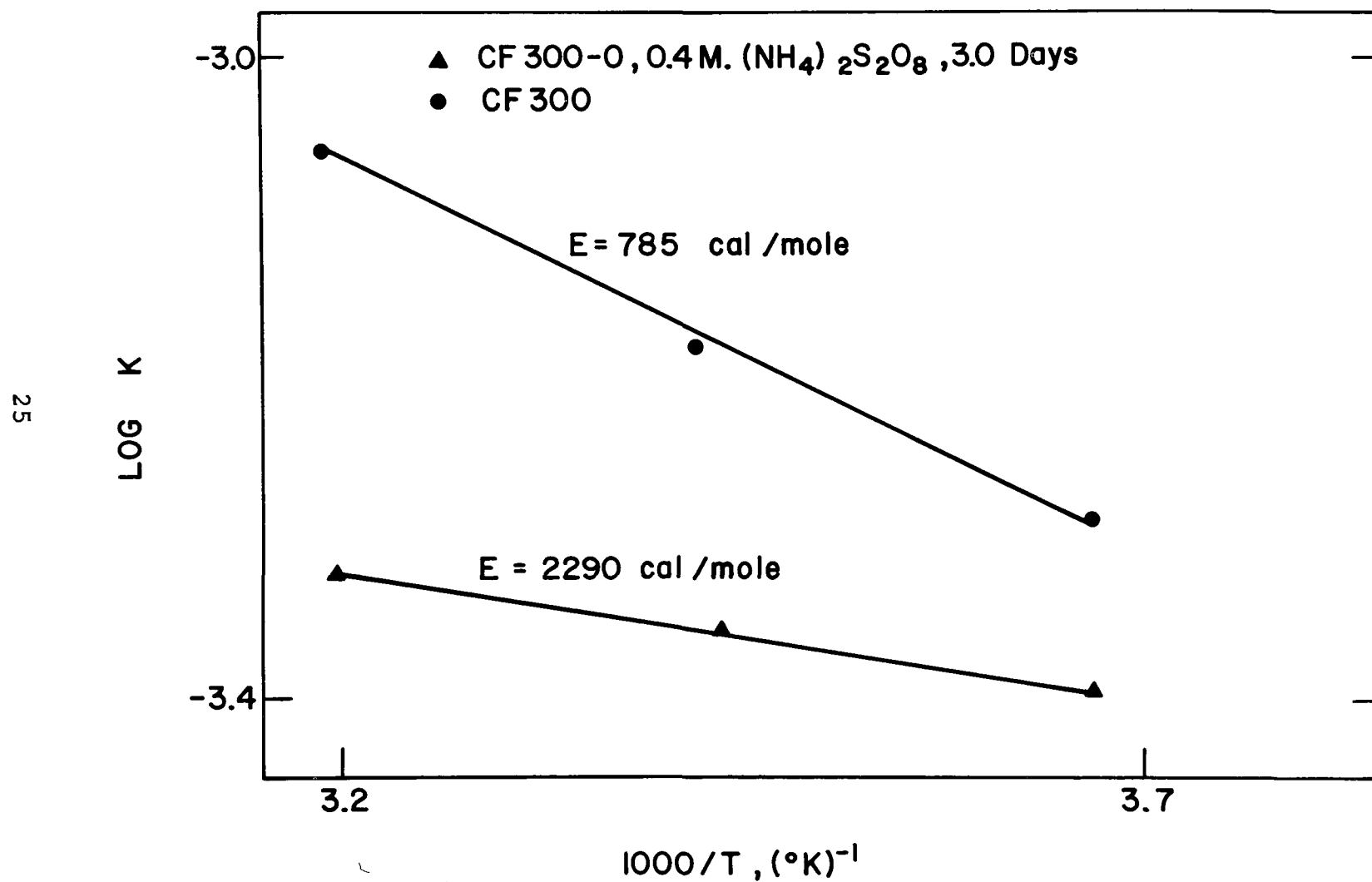


FIGURE 13 ARRENIUS PLOT FOR THE ADSORPTION OF DEXTROSE ON CF300 IN AQUEOUS SOLUTION, PARTICLE SIZE RANGE 2.38-2.83 mm.



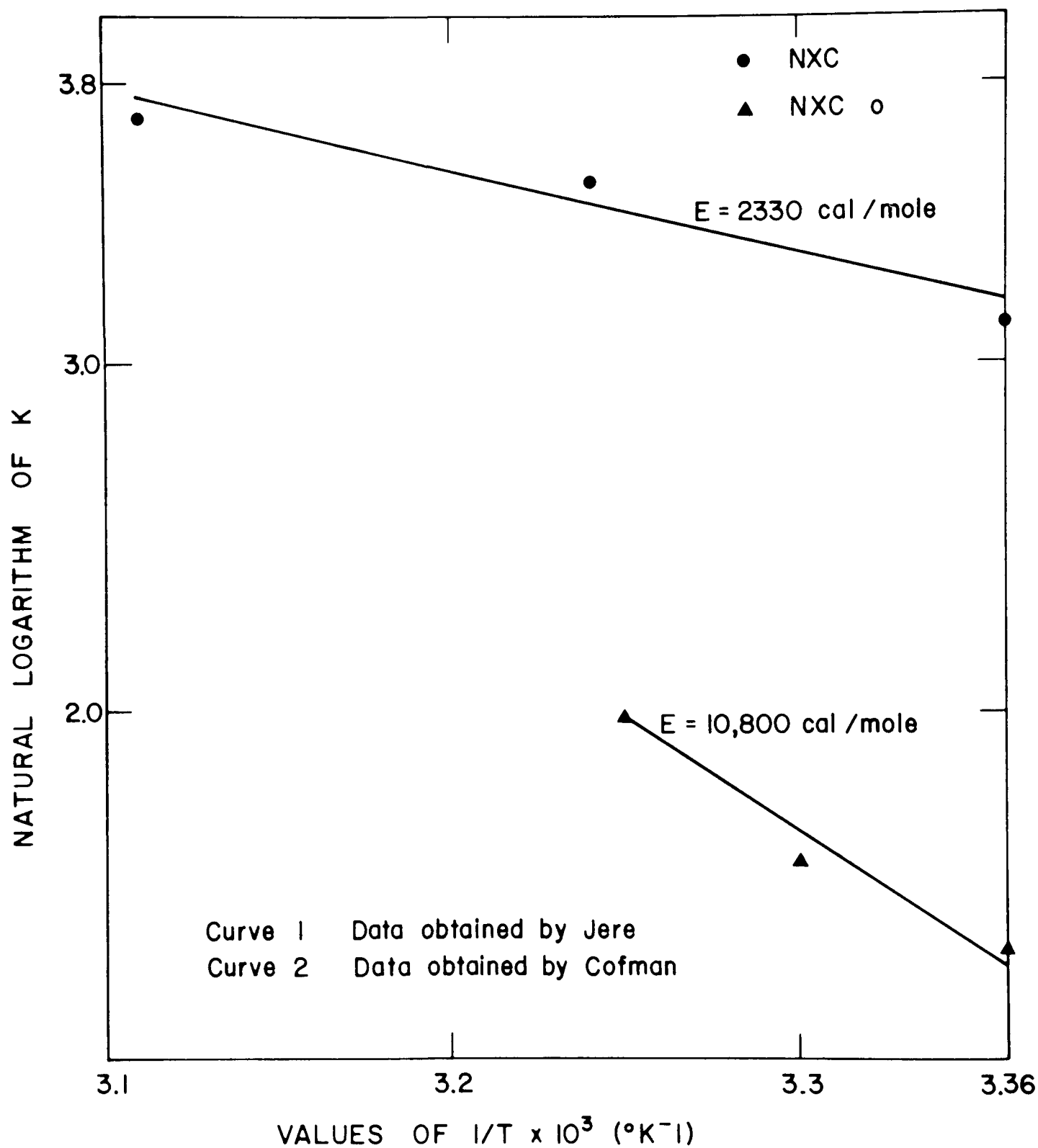


FIGURE 14 DETERMINATION OF ACTIVATION ENERGIES

carbons NXC and NXC-O. In each case, it is evident that oxidation increases the apparent activation energy.

It is interesting to speculate how a detailed knowledge of the kind of phenomena reported here might be harnessed to produce more efficient waste treatment. For example, when more knowledge becomes available as to the specific chemical components in primary and secondary effluent it may become possible to use carbons treated in different ways to selectively remove different classes of chemical compounds. On the basis of the present results, it would appear desirable to contact effluent with non-acidic carbon (say vacuum outgassed or reduced) to remove compounds similar to phenol and nitrobenzene as well as with oxidized carbon to remove compounds similar to urea. The results reported here should serve as motivation to study the influence of acidic groups on the sorption of other classes of compounds like proteins, amino acids, fats, sugars, tannins, lignins, etc.

SECTION VI

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