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Effects of acidic surface oxides on the adsorption properties of carbon

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EFFECTS OF ACIDIC SURFACE OXIDES
ON THE ADSORPTION PROPERTIES OF CARBON

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ABSTRACT

Previous works show that the nature of the carbon surface plays an important role in the adsorption process. Among the functional groups on the surface, the acidic oxides are the most significant. This work shows that these acidic oxides groups may be modified at will by chemical or thermal treatment. Adsorption studies with low concentration phenol and sodium benzenesulfonate onto three types of active carbon and channel blacks show that the adsorptive capacities are markedly reduced when the surface oxide concentration is increased. The adsorptive capacities are restored upon reduction of the concentration of acidic oxide groups. Good correlation is obtained between the total acidic groups present on the surface and the percentages of adsorbent surface area covered by the adsorbates. Similar effects on the adsorption of phenol at high concentration are observed but are not as pronounced and distinct as in low concentration.

The results suggest that phenol molecules are adsorbed flat on the surface of the adsorbent at low concentration and reorient themselves into the end-on position as the concentration is increased. Benzenesulfonate molecules appear to be adsorbed in the vertical position even at low concentration, and addition of traces of Ca^{++} greatly enhances its adsorption.

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INTRODUCTION

Recently, considerable research has be made toward studying the advanced treatment of waste water. Among the techniques and process being considered, the adsorption of the biochemically resistant pollutants with activated carbon have attracted numerous studies (1,2,3, 4,5,6,7,8,9,10). This is mainly due to the commercial availability of activated carbon, its high adsorption capacities and its affinity for a broad spectrum of chemical compounds.

These investigations have found the adsorption of organic pollutants from aqueous solution onto several different kinds of carbon to have differed significantly in equilibrium capacities. Some of these results suggest that the differences in adsorptive capacity between various types of carbon may be due to differences in specific surface area (1), in pore-size distribution (11), or differences in the nature of the surface and in the population and types of functional groups on the surface (11,12).

Commercial active carbon and carbon black frequently contains impurities, some of which are purposely added during the manufacturing process. These impurities differ from one carbon to another depending on the conditions

under which it was processed and on the process itself.
The most important and best known among the surface compounds of carbon are those with oxygen and sulfur, although chlorine and hydrogen can also combine with elemental carbon (11). Of these surface compounds of carbon the surface oxides have been studied most, specially the acidic surface oxides (13,14,15,16,17,18,19). Basic surface oxides have also been found on the surface of the carbon (13,20).

Graham (11), in his study of the adsorptive capacity of Graphon and some commercial active carbons, found that acidic chemisorbed oxygen on the surface of the carbon do play a significant role in adsorption from aqueous solution. The work revealed that acidic oxides groups tend to reduce the adsroptive capacity of carbon with metanil yellow, an anionic dye, while the adsorption of methylene blue, a cationic dye, did not appear to be affected. Graham attributed this behavior to the repulsive interaction between the anionic metanil yellow and the acidic oxides on the surface. He suggested further that this type of interaction might be expected for anionic adsorbates in general.

Some of the acidic oxide groups on the surface of the carbon have been identified and reported (13,14,15, 16,17,18,19,20,21). These investigations used either

reactions of organic chemistry or infrared spectrophoto-
metry to characterize oxygen chemisorbed on carbon.
However, of the many techniques for characterizing the
acidic surface oxides of carbon, the method used by
Boehm, Diehl, et al (13) has been employed in this work.
In this technique, four different types of acidic surface
groups are characterized as I) a strongly acidic carboxyl
group, II) a more weakly acidic carboxyl group, III) a
phenolic hydroxyl group, and IV) 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 reactions with bases of different
strength. Thus group I is neutralized by each of the
bases $NaHCO_3$, Na_2CO_3, NaOH and $NaOC_2H_5$; group II is neu-
tralized by Na_2CO_3, or stronger bases but not by $NaHCO_3$,
etc. It is thus possible to identify the acidic surface
oxides present on a given sample of carbon by simple titra-
tion with different bases.

Most commercial-type carbon contains oxides groups on
the surface, but additional amount may be introduced by
oxidation in air or pure oxygen at elevated temperature or
by mixing the carbon sample with aqueous solution of

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oxidizing agents like $NaOCl$, $KMnO_4$ or $(NH_4)_2S_2O_8$ (13).
It is also possible to remove the acidic functional groups
totally or partially by reduction or vacuum outgassing at
elevated temperature. Boehm, et al (13) also reported
that the ratio of the different quantities of bases neu-
tralized bear simple, whole number relationship to one
another. With samples that were oxidized in oxygen and
elevated temperature, the ratio is 1:2:3:4, suggesting
the presence of equivalent quantities of at least four
different types of acidic groups of definite acidities.
With samples obtained through "wet" oxidation, the quan-
tities of base required for neutralization are in ratios
of 2:3:4:5. However on subsequent heating to about $200^{o}C$,
the ratios were again found to be 1:2:3:4.

Another significant factor that needs consideration
in the adsorption from liquid phase onto solid phase is
the orientation of the adsorbed molecules and the thick-
ness or number of molecular layers of the adsorbed film.
Experimental results showed that in the micromolar region,
data obtained for most of the common pollutants conform
very well with the Langmuir equation (1), suggesting that
the adsorbed film is monomolecular. Studies with the
phenol-water system have shown that the phenol isotherm
displays two plateaus in adsorption on carbon (1,6), but

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usually give a S-type isotherm when adsorbed on a polar
substrate, e.g., alumina, from a polar solvent (22).
The latter behavior has been interpreted by Giles, MacEwan,
et al (22) as a monofunctional attraction toward the polar
substrate arising from the hydroxyl group of the phenol.
Here the phenol molecules were viewed to be adsorbed end-
on, standing side by side to be more stable, thus result-
ing in more molecules to be adsorbed on the surface. This
account for the S-shaped isotherm. Data from experiment
(1) have shown however that phenol isotherm for adsorption
on carbon at low concentration appears to be Langmuirian
in character and not S-shaped. This suggests that the
attraction of phenol for the carbon lies probably in non-
polar forces operating over the whole phenol nucleus.
This lead Giles, MacEwan, et al (22) to suggest that the
second step in the isotherm may represent the reorienta-
tion of the phenol molecules from the prostrate to the
end-on position. Or the second plateau may represent a
second condensed monolayer formed on top of the first
(1,6).

Giles, MacEwan, et al (22) also reported that aromatic
sulphonic acids appear to be monofunctional toward graphite
in water, probably because the very high attraction of the
sulfonate group for water draws this group as far as

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possible into the water phase, and thus only the opposite
unsulphonated end of the nucleus is in contact with the
graphite. Zettlemoyer, et al (24) in studying the adsorp-
tion of calcium ions to surfactant film on Graphon,
reported that trace amounts of calcium strongly enhance
the adsorption of dodecylbenzene sulfonate onto Graphon.
Apparently, the adsorption of Ca^{++} reduces the repulsion
between the sulfonate anions so that close packing can
occur.

OBJECTIVES

The primary objective of this project is to employ
the techniques and characterization used by Boehm, Diehl,
et al (13) to study the effects of the acidic surface
oxides groups on the adsorption of various adsorbates onto
carbon in aqueous solution. Attemps will also be made to
isolate individual functional groups on the surface of the
carbon so as to shed light to the role played by each
group individually and collectively. It is clear that
this information will permit better materials to be
designed for adsorbing specific compounds and provide the
basis for increasing the adsorptive capacity of presently
available materials, either through modification in manu-
facturing technique or by special treatment to provide

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the "right kind" of surface groups. In addition, this
information will point the way towards better means of
regeneration for spent adsorptive materials by identify-
ing which surface groups must be replaced, which can be
re-activated, etc.

SELECTION OF ADSORBATES

Phenol and Sodium Benzenesulfonate were the two
adsorbates used in this work. Both are common pollutants
of waste water and techniques for the quantitative analy-
sis of both compounds are relatively fast and simple.
Considerable amount of work has already been done with
phenol-carbon system in aqueous solution, which would be
very useful for comparison and reference purposes. Ben-
zenesulfonate has a highly polar sulfonate group, making
it ideal to study the effects on its adsorption onto the
carbon by the surface functional groups on the surface.

Both adsorbates used in this work were of reagent
grade. Impurities in phenol include 0.040% of residue
after evaporation and 0.15% of preservative (H_3PO_2).
Sodium Benzenesulfonate used were of the grade recrystal-
ized from methanol.

SELECTION OF THE ADSORBENTS

Three types of microcrystalline carbon were used in this work. They are all commercially available and were procured directly from their respective manufacturers. They were (a) Activated carbon "Columbia LC325" (Union Carbide Corp.), (b) Activated carbon "Darco S51" (Atlas Chemical Co.) and (c) Pelletized channel black "Black Pearl 607" (Cabot Corp.).

Columbia LC325 was selected because extensive works were already made with this carbon (1,2,3,4). These works were also carried out in conjunction with advanced waste water treatment and deal mostly with kinetics and equilibria of the adsorption of biochemically resistant materials onto carbon. It thus represent a valuable guide and reference for this work. Black Pearl 607, a channel black, represented a different crystalline form and activation, which may yield results useful for evaluation and comparison purposes. Concurrent work (25) was also being conducted with this carbon in the same general direction, thus Black Pearl 607 also presented a bridge for eventual comparison of data obtained. Darco S51, another activated carbon with high adsorptive capacity, was used together with the LC325 with the main purpose of reproducing whatever results were obtained with the LC325.

Considering that both carbon were commercial samples,
this arrangement were followed to minimize any chances of
running into a special case and besides, it also provide
valid ground for eventual generalization of the results.

ANALYTICAL PROCEDURES

A. Analysis of Surface Oxides

The determination of the acidic surface oxide groups
consisted of equilibrating 0.500 gram of the sample with
50.0 ml. each of 0.1000 Normal $NaOC_2H_5$, NaOH, Na_2CO_3 and
$NaHCO_3$ solution for three days. A 10-ml. aliquot is then
pipetted out and titrated with 0.0500N HCl, using phenol-
phthalein as indicator in case of $NaOC_2H_5$ and NaOH, and
methyl orange in case of Na_2CO_3 and $NaHCO_3$.

B. Analysis of Adsorbates Concentration

Determination of the concentration of solution is
done by ultraviolet spectrophotometry. Initial work was
done with the Beckman DK-2A, double-beam spectrophotometer
but owing to its frequent breakdown, most of the data were
obtained through Spectronic 505 (Bauch & Lomb, Inc.),
which is also a double-beam spectrophotometer. The photo-
metric accuracy of this equipment (-.005 at 0.4A) is well
within the tolerable limit of the experiment.

Determination of phenol solution at high concentration was carried out with a differential refractometer (Brice-Phoenix Differential Refractometer Model BP-2000V) using a green filter (546μm).

C. Determination of Surface Area

The specific surface areas of the different samples were obtained from N_2 adsorption by the B. E. T. method. The sample was first prepared by degassing at 10^{-6}mm Hg of vacuum and 110°C before subjecting it to adsorption measurement. A mercury manometer was used in the measurement of the nitrogen pressures.

EXPERIMENTAL PROCEDURES

A. Preparation of the Adsorbates

Stock solutions of both adsorbates were prepared at a standard concentration of 0.020 molar by weighing appropriate quantities of the chemicals and dissolving them in suitable volume of doubly-deionized water.

To prepare the solution for an isotherm run, standard solution was pipetted out from the stock solution and properly diluted to give a working solution. This working solution was then further diluted into the various concentration desired.

B. Preparation of the Adsorbents

The first step in the preparation of the adsorbents consisted of stirring the activated carbon (both LC325 and S51) for 24 hours in 0.1N HCl solution in order to remove alkaline impurities, followed by thorough washing with doubly-deionized water. The channel black (P607) however was merely stirred in doubly-deionized water for 24 hours. All samples were then dried overnight at 110°C before use in any experiment or any further preparatory treatment. These leached samples are henceforth referred to as LC325 (or L), S51 (or S) and P607.

The surfaces of the carbons were modified by "wet" oxidation and reduction. Oxidation was carried out by stirring about 20 grams of carbon samples in 500 ml. of $(NH_4)_2S_2O_8$ solution. Different concentrations of $(NH_4)_2S_2O_8$ solution were tried at various lengths of oxidizing time (Table I & II). These oxidized samples were then washed thoroughly with doubly-deionized water and dried at 110°C for 24 hours. (These oxidized samples were referred to in this work as L- followed by a number or S- followed by a number). In order to standardized the preparation and make the results more significant, only the L-12 and S-8, which were both oxidized with saturated $(NH_4)_2S_2O_8$ solution (about 2.5M) for 3 days were selected

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for additional treatment and experiment. (The oxidation of the carbon adsorbents with saturated solution of $(NH_4)_2S_2O_8$ is exothermic, and care must be exercise during the first few hours of such a treatment. It is recommended that the solution be cooled by running water). These two samples are henceforth referred to as LC325 O and the S51 O. Only one sample was prepared for Black Pearl 607. The oxidized sample (P607 O) was prepared by oxidizing it with 0.5M $(NH_4)_2S_2O_8$ solution for 2 days, followed by thorough washing with doubly-deionized water and dried at $110^\circ C$ for 24 hours. Black Pearl 607 had a tendency to turn greasy and broke down into very fine particles if it was oxidized too long or when the concentration of the oxidizing agent used was too strong.

The reduction of the samples consisted of mixing about 15-20 grams of the above oxidized samples with zinc amalgam (which consisted of 50 grams of 10 mesh granular zinc covered with mercury) and then covering with about 150 ml. of concentrated HCl. The reduction was carried on for one week, followed by thorough washing with doubly-deionized water and then dried at $110^\circ C$. These samples are referred to as LC325 OR, S51 OR and P607 OR.

Further preparation of the samples consisted of heating the oxidized samples at elevated temperature and

high vacuum (10^{-6}mm Hg). This was done by spreading the samples in a vycor tube about 1" in diameter and 10" long, one end of which is sealed and the other end connected to a high vacuum system. The tube was inserted into a high temperature furnace, and the temperature was measured with an iron-constantan thermocouple and a potentiometer. Each sample was prepared by first putting it under vacuum, then heating it up to the desired temperature and, let stand for 24 hours. In removing the samples, it is very important that the sample tube be cooled down to room temperature first before the vacuum is broken. The vacuum system here consisted of a mechanical vacuum pump series with a single stage mercury diffusion pump. The system was capable of producing a vacuum of 10^{-6}mm of mercury. Of the samples that were vacuum outgassed, only the L-12 and S-8 outgassed at 890°C for 24 hours were used for further experiment. These are referred to as LC3250D and S51 OD (Table III).

Analysis for the surface oxide groups on each of the above treated samples were made with the technique mentioned earlier, and the results were reported in Table I, II & III. It should be noted that the amount of time allowed for the different bases in contact with the carbon samples was an important factor in reporting the base consumption or the amount of surface oxide groups present.

This equilibrium time was also standardized to 3 days in this work.

C. Procedures for Adsorption Studies

Adsorption studies with these samples were conducted in batch process with both phenol and benzenesulfonate solution. Solutions of different concentration were prepared at 2,000 ml. each from the working solution by dilution. The solution was then evenly divided among four 500 ml. bottles using volumetric flasks for measurement. Usually three samples of one type of carbon which have been treated differently were run in the same batch, with the fourth series of solution being used for calibration purpose. This arrangement provided identical conditions for one set of adsorption isotherms. Comparison of results was easy and direct, and errors, either environmental or mechanical were also minimized. Appropriate amount of adsorbents must be used in each case, and after some preliminary runs, the following quantities were used in this work. To each 500 ml. of phenol solution, 0.050 gram of the unmodified and OD, and 0.100 gram of the O and OR samples were added; for benzenesulfonate solution, 0.050 gram of the unmodified was also used, but for the O and OR, 0.150 gram were used for each 500 ml. of the solution.

After the appropriate amounts of samples were introduced into the solution, the reaction bottles were put into a water bath keep constant at $30 \pm .5^{\circ}C$. and equilibrated for 3 days with occasional shaking (about once a day). Prolonging the equilibrium time to 6 days gave less than 5% increase in adsorption as compared to that obtained with 3 days. To prevent any interference during ultraviolet analysis by any left-over impurities on the samples, additional samples from each were weighed out and introduced into 500 ml. of doubly-deionized water and also equilibrated for 3 days. The equilibrium supernatants were then used as reference solutions during the determination of the concentration using ultraviolet spectrophotometry.

All low concentration runs on both phenol and benzenesulfonate were done with the Spectronic 505, a double-beam spectrophotometer using a set of 10 mm. quartz cells.

For the range of concentration studied, the phenol solution conformed excellently to the Beer-Lambert Law, showing good proportionality of absorbance to concentration at the wavelength used. For benzenesulfonate solution however, there was a slight deviation at the higher concentration range.

Phenol showed an adsorbance peak at 270 millimicron,

but benzenesulfonate did not show a peak at the range
studied. However, a plateau of high absorbance was
observed at short wave length and measurement were made
at 216 millimicron, the wavelength corresponding to the
beginning of the level part of the plateau (26).

Determinations of phenol at high concentration ex-
periments were measured with a differential refractometer.
Working within this range neccessitates the involvement of
large quantity of carbon samples to effect a change in
concentration large enough to be measured within tolerable
accuracy. In this case 1.00 gram of samples was used for
a 100 ml. solution with concentration ranging from 0.100
to 0.400 molar. The saturated concentration of phenol
solution is 0.8955 molar (6).

Kinetic data for the adsorption of adsorbates onto
the carbon was conducted similar to an adsorption run
except aliquot portions of the solution were removed at
different time interval. Calculation in this case were
corrected to take account of the changes in volume due to
sample removal. These runs were also conducted in 500 ml.
bottles, and the amount of adsorbent used in each case
also corresponds to the amount used in the adsorption
studies.

RESULTS AND DISCUSSIONS

A. Samples and Their Characterization

One of the main problem encountered in this work was the preparation and treatment of the adsorbents. Obviously any subsequent results and observations made in this study depended heavily on their proper characterization. Table I and II list the numerous samples that were treated and characterized as to surface-oxide groups. It shows that the amount of functional groups put onto the surface of the adsorbent depends on the strength of the oxidizing agent used and the length of oxidation time. The general trend indicates a proportional increase of surface-oxide groups for increasing concentration of oxidizing agent and length of contact time. In the characterization of the groups itself, the amount of base required for neutralization increases as the equilibrium time is prolonged, suggesting that the attainment of equilibrium is a slow process. However, an increase on the concentration of the bases used was reported to have little or no effect on the base consumption (13).

Ratios of the base consumption are also listed on the last column, and although these figures do not bear the simple, whole number ratios as reported by Boehm,

Diehl, et al (13) for this type of oxidation treatment, they show a definite trend that such a ratio was indeed possible and probable. Possible explaination for such discrepancies may be due to the fact that Boehm, Diehl, et al (13) worked with pure sugar charcoal while technical grade commercial samples were used in this case. It is apparent however, that four types of acidic oxide groups do exist, though again not in equivalent quantity as reported (13). It appeared instead that group I and III, or the strong carboxyl group and the phenolic group are the predominant groups.

One of the objectives of this work is to isolate the different groups of surface oxides that were characterized and study its role in the adsorption process. It was reported that during pyrolysis of the acidic surface oxides, each individual group was decomposed at a different temperatures (13,14). Table III lists the results obtained in this attempt. The results show that the decomposition occured to all the groups to a certain extent, and no clear preference of any individual group. Pyrolysis at $890^\circ C$ did resulted in an apparent complete decomposition of group II and IV, but then the remaining groups I and III were also reduced significantly in quantity for them to be of any value in the study for their roles in the adsorption.

These samples however provided excellent examples of how a low capacity adsorbent may be improved by removal of surface oxide groups.

B. Kinetics Studies

Prior to any adsorption equilibria studies, the kinetics of adsorption was conducted with most of the samples involved. The results are shown in Figures 2, 3 and 4. No efforts were extended to take the kinetics during the first few hours of the uptake. Some of these were already studied by Morris & Weber (1) who reported that intraparticle diffusion of solutes in the internal capillary pores of the carbon is the rate controlling factor. It was also shown that there was an abrupt decrease in the rate as adsorption proceeds and a slow approach to final equilibrium. Apparently Figures 2, 3 and 4 represent the adsorption on its slow approach to equilibrium. Adsorption results obtained for 6 days showed an increase in uptake of less than 6% as compared to those for 3 days. Of utmost importance to this work however is not whether equilibrium was in fact attained but that all samples studied had approached equilibrium to the same extent. This would provide ground for a meaningful comparison of adsorptive capacities between

the various samples involved. Besides, practical adsorption works are usually terminated well below the equilibrium point for maximum efficiency.

C. Adsorption of Phenols

As was already obvious in the kinetic runs, the adsorption isotherms at low concentration obtained from the different samples with phenol exhibited significant differences in adsorption capacities as shown in Figures 5 and 6. In both cases, the effect of oxidation appeared to have reduced the adsorption capacities of the carbon for phenol by a factor of 2 to 3 on a per gram basis. Using the values of specific surface area obtained from N_2 adsorption by the B. E. T. method, Figures 7 and 8 were prepared from the same data with the amount adsorbed expressed in a per unit surface area basis. It is apparent that the adsorption isotherms are basically identical with those on Figures 5 and 6, suggesting that the differences in adsorption capacities were not due to different surface area. It must be remembered however that these furface areas included micropores and capillaries accesible to the smaller nitrogen molecules, but not necessarily accesible to the larger phenol molecules.

Dependence of adsorption on the nature of the adsor-

bent surface, although not specifically studied, has been reported before (11). Thus, the results of reduction or vacuum outgassing at elevated temperature of the oxidized samples, which in effect removed or destroyed some of the surface oxide groups, tends to restore or at least increase the adsorptive capacities of the samples. Considering that no significant change in specific surface area was observed in such a treatment, these results indicate that these functional groups are directly responsible for the difference in adsorptive capacity. This is in agreement with an earlier work which showed isotherms of similar type of carbon (LC325) used in this work but oxidized to a higher total acidity exhibiting an even lower adsorption capacity (25).

Phenol adsorption at high concentration were also conducted with two of the carbons (LC325 and P607); the results are shown in Figures 9 and 10. These results indicate that the effects of the functional groups on the adsorption capacities were the same at high and low concentration. However the differences in this higher concentration range were not as large as those exhibited for lower concentrations. The differences in these case were only about 25% for P607 and from 50 to 100% for LC325. It is interesting to note though that the iso-

therms of the oxidized and reduced samples can hardly be differentiated for P607 while for LC325 there was even a reversal, with the oxidized samples showing a greater adsorptive capacity than the reduced samples. No explaination was available at this point for such discrepancies although a cumulation of errors was suspected. The results also differ from the results of Coughlin & Ezra (25) that a high concentration the isotherms did not appear to be influenced strongly by the functional groups. It was reasoned that at high concentration the molecules are adsorbed in the vertical or end-on position with the forces of interaction between the phenol molecules themselves affecting the adsorption more than that between the phenol and the functional groups. Still another complicating problem which arose in working at this concentration was the occurrence of multilayer adsorption. Data available at this point were inadequate and no attempt has been made to resolve the problem.

In the lower concentration region, the isotherms appeared to be of Langmuirian type. The plateaus of the different isotherms were visually determined at an arbitrary equilibrium concentration of 250 micromoles per liter and are listed in Table V. Taking the cross-sectional area of the phenol molecule laying flat as 41.2

Angstroms squared, the approximate surface coverages of
the different adsorbents by phenol were calculated and
are listed in Table VI. The fact that the surface cover-
age range from 10 to 40% suggested that the adsorption
was well below the monolayer region.

The data for the lower concentration range for phenol
were also fit to the Langmuir equation for monolayer
adsorption,

$$X = \frac{X_m bC}{1 + bC}$$

$$\text{or} \quad \frac{C}{X} = \frac{1}{X_m b} + \frac{C}{X_m}$$

where C = equilibrium concentration

X = amount of solute adsorbed per unit weight of
adsorbent

X_m = value of X for complete monolayer coverage

b = Constant in Langmuir equation, expressive of
energy of interaction with surface

A plot of C/X versus C revealed two different straight
lines with different slopes for each isotherm. The break
in the line, i.e., the point where the slope changes,
appeared to occur at 70 micromoles per liter for LC325 and
at 120 micromoles per liter for S51. These concentrations
are well below the ranges where the second plateau of a
phenol isotherm occur. The slopes of the lines were
obtained and tabulated in Table VII. The results shows

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that the break lowered the slope by about 50-60%. Since the reciprocal of the slope is X_m, the amount of adsorbate required for a complete monolayer coverage, the results suggested that either the surface area available for a monolayer adsorption had suddenly doubled, which is not probable, or the packing or orientation of the adsorbed molecules had changes. Giles, MacEwan, et al (22) reported that although the phenol molecule is usually thought adsorbed end-on because of the monofunctional attraction of the hydroxyl group toward polar substrate, experimental isotherms at low concentraion appeared to be of Langmuir type. The presence of a second plateau at a higher concentration lead them to suggest that at low concentration, the attraction of phenol for carbon probably lies in non-polar forces operating over the whole phenol nucleus. The second step in the isotherm represents a reorientation of the phenol molecules from the prostrate to the end-on position, thus uncovering a portion of the original surface of the carbon. Ottewill and Tiffany (23), in a study of the adsorption of long chain acids onto rutile, showed that the reorientation of the unsaturated acids adsorbed on the surface was characterized by a sharp break in the slope of the Langmuir plot. Figure 11 and 12 showed a similar change in slopes suggesting the reorien-

tation of the phenol molecules adsorbed on the surface
of the carbon substrate. The change appeared to start
at a concentration of about 70 micromole/liter for the
LC325 samples and 120 micromoles/liter for the S51.
Using the cross-sectional area of the phenol molecule
laying flat on the surface as 41.2 Angstroms squared, and
that of a vertical or end-on position (the molecules were
considered to be standing straight up, thus giving a mini-
mum cross-sectional area) as 18 Angstroms squared, the
surface area of such a monolayer was calculated and is also
tabulated in Table VII. The reasonably good agreement bet-
ween the surface areas obtained by the two sets of slopes
well supports the theorized reorientation of the adsorbed
phenol molecules.

D. Adsorption of Benzenesulfonate

Adsorption studies of benzenesulfonate were also
conducted. Some kinetic studies were also carried out
and are reported in Figure 4. Figures 13, 14 and 15 show
the results of the adsorption studies with benzenesulfo-
nate with the various samples. These results revealed the
same effect on the adsorptive capacities of the adsorbent
by the functional groups as with the phenol. In fact, as
shown by the reduction of adsorptive capacities by factors

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from 3 to 14 for oxidized samples, the effects seemed to
be more pronounced. The reduction of the samples also
tended to restore the adsorptive capacities but, except
for P607, fell well below the original capacities.

The adsorption isotherms in Figures 13 and 14 appeared
to be Langmuirian, while the Figure 15 isotherm was of the
S-type. This was not surprising since Giles, MacEwan, et
al (22) showed that aromatic sulfonic acid appeared to be
monofunctional toward graphite in water. It seemed that
the high attraction of the sulfonate group for water draws
this group as far as possible into the water phase, and
thus only the opposite unsulfonated end of the nucleus is
in contact with the graphite. In this way the strong
intermolecular forces between their hydrophobic nucleus
can exert their maximum effect; that is, a solute molecule
is more stable adsorbed adjacent to other already adsorbed
molecules than in isolation by itself. This implies that
the more solute is adsorbed, the easier it is for additio-
nal amounts to become fixed. This phenomenon leads to an
S-shaped isotherm. Further, they indicated that whenever
an S-shape isotherm is obtained with any aromatic solute,
the adsorbed molecules are oriented perpendicularly to
the surface, but not vice versa. Thus, despite the Lang-
muirian shape of the isotherms in Figures 13 and 14, the

orientation of the benzenesulfonate molecules are theorized to be perpendicularly adsorbed to the surface.

In all cases, the monolayer capacities of benzenesulfonate were very much smaller than they were with phenol. This is somewhat surprising considering that phenol molecules were adsorbed flat on the surface of the carbon adsorbates and hence should be occupying more space. Morris & Weber (1) noted similar results and suggested that this decreased capacity may be due to mutual repulsion by the ionic sulfonate groups so that they are not able to pack as closely to each other as can phenol molecules.

E. Effects of Calcium Ions on the Adsorption of Benzene Sulfonate

The adsorption studies of benzenesulfonate had shown that while the adsorbate molecules were adsorbed perpendicularly to the surface, thus occupying minimum of surface space available for adsorption, the mutual repulsion between the highly polar sulfonate groups prevented any close packing from occuring. Zettlemoyer, et al (24) reported that traces of calcium ions greatly enhanced the adsorption of sodium dodecyl sulfate and sodium dodecylbenzene sulfonate onto Graphon. Apparently the adsorption of calcium

ions reduces the repulsion between the sulfonate anions
so that closer packing can occur. Experiments in this
direction were conducted with benzenesulfonate as the
adsorbate and the results are shown in Figures 16, 17 &
18. As expected, there was a general increase in the
adsorption of benzenesulfonate when traces of Ca^{++} were
added. It is interesting to note that while the increase
in adsorptive capacity for an untreated sample (LC325 in
Figure 16) was a mere 15 to 20%, the increase for the
treated samples (S51 OR in Figure 17 and P607 O in Figure
18), with the same amount of Ca^{++} added, was about 200
and 50% respectively. These results seem to indicate that
while the repulsive forces between the adsorbates molecules
were reduced by the addition of Ca^{++}, it is probable that
the repulsive forces between the surface oxide groups and
the adsorbed molecules were also correspondingly reduced.
Unfortunately, the data available were insufficient to
draw any positive conclusions.

Figures 19 shows the adsorption isotherm of phenol
with and without the presence of Ca^{++}. As expected, the
results show no change in the adsorptive capacity, thus
further strengthening the proposition that the attraction
of phenol for the carbon lies in non-polar forces operating
over the whole phenol nucleus.

F. Total Acidity and Area Coverage

In order to correlate the data, the plateau values for the adsorption of phenol and benzenesulfonate were obtained by reading it from the graphs at two arbitrary equilibrium concentration well within the plateau region. Since these adsorption values corresponded to the monolayer adsorption of the adsorbates, the surface area of the adsorbent covered by these adsorbates may be calculated by using 41.2 and 22.3 Angstroms squared as the cross-sectional area of the phenol and benzenesulfonate molecules respectively. Phenol molecules were considered to be adsorbed flat on the surface of the carbon adsorbent while the benzenesulfonate molecules were assumed adsorbed in the vertical or end-on position. These results are shown in Table V and VI together with the total acidity ($NaOC_2H_5$ consumption) of the adsorbents and the specific surface areas as determined by nitrogen adsorption using the B. E. T. method. As shown in Figures 20 and 21, the calculated percentages of adsorbent surface area covered by the adsorbates (tabulated in the first two columns in Table VI), display a fairly good correlation with the total acidity of the adsorbents. An earlier report on this correlation (25) is included in Figure 20. A comparison of the two results showed excellent similarity

in the correlation curves of the two parameters, except
that the curve was shifted upward and to the right.
This discrepancy may probably be attributed to the cha-
racterization of the acidic oxide groups. It was reported
that the samples used in the lower curve were neutralized
with the base for 24 hours (25), while in this work, the
neutralization took 3 days. It is thus possible to increase
the total acidity accounted for by prolonging the neutra-
lization time. The effect of this will shift the lower
curve to the right.

Figure 21 showed the same correlation with benzene-
sulfonate as the adsorbate. While a similar trend was
displayed, no conclusive relationship was projected due
to the scatter in the data.

CONCLUSIONS AND RECOMMENDATIONS

This study shows that different quantity of acidic
surface oxides may be put onto the surface of the carbon
by simple chemical treatment. These surface oxides may
also be reduced or removed by either chemical or thermal
treatment. Attempts to isolate individual group of
these surface oxides with thermal decomposition under
vacuum have failed, but other techniques such as chemical
treatment for selective blocking or neutralization of a
particular group are worth trying.

The results show the capacity of carbon adsorbent
to pick up anionic adsorbates such as phenol and benzene-
sulfonate to be definitely related to the concentration
of acidic oxide groups present. In general, the lower
the concentration of acid surface oxides, the higher the
adsorptive capacities. Adsorbents with low acidic oxide
groups may be obtained by either wet reduction with zinc
amalgam or vacuum outgassing at elevated temperature.
The degree of adsorption also depends on the types of
adsorbates and adsorbents involved. Thus activated car-
bon exhibits higher capacity than the channel black, and
both adsorbents show larger capacity for phenol than for
benzenesulfonate. Results show that the latter phenome-
non is due to the strong mutual repulsion between highly

polar sulfonate groups of the adsorbates, and that this interacting forces may be reduced by the addition of traces of Ca^{++}. The addition of Ca^{++} is also believed to reduce the mutual repulsive forces between the functional groups and the adsorbates. Additional experiment with the Ca^{++} is recommended to provide a positive conclusion.

The results also show the reorientation of the phenol molecules from the prostrate to the end-on position to have occurred at a relatively low concentration. Some differences in the adsorption capacities are also detected with phenol at high concentration. Again, additional experiment on this is recommended.

APPENDIX

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TABLE I. *Neutralization of Acidic Surface-Oxides*

| SAMPLE | CONC.* MOLAR | OXID.* DAYS | EQUIL.* DAYS | BASES USED, meq/100g. | | | | RATIO* |
				NaOEt	NaOH	Na_2CO_3	$NaHCO_3$	
L			7	144	105	75	77	
L			2	52	54	21	20	
L-2	0.05	7	7	200	115	57	95	4.2/2.4/1.2/2
L-3	0.1	7	7	233	109	34	46	10 /4.8/1.4/2
L-4	0.2	14	7	270	180	105	65	8.2/5.6/3.2/2
L-5	0.3	8	7	275	222	110	75	7.4/6.0/2.8/2
L-6	0.2	20	2	185	110	54	22	16 /8.0/4.8/2
L-7	0.2	22	2	155	109	49	35	8.8/6.2/2.8/2
L-8	0.2	30	1	128	110	40	20	12 / 11/4.0/2
			2	175	125	45	28	12/8.6/3.2/2
L-9	SAT	3	2	322	380	257	187	3.4/4.0/2.8/2
L-10	1.0	30	2	279	258	166	107	5.2/4.8/3.0/2
			3	313	262	184	122	5.1/4.3/3.0/2
			5	311	262	167	115	5.4/4.6/2.8/2
L-11	0.2	180	3	162	121	79	60	5.4/4.0/2.6/2
L-12	SAT	3	3	310	292	205	150	4.2/3.8/2.7/2

*Note: refer to Table II

TABLE II. *Neutralization of Acidic Surface-Oxides*

SAMPLE	CONC. MOLAR	OXID. DAYS	EQUIL. DAYS	BASES NaOEt	USED, NaOH	meq/100g. Na$_2$CO$_3$	CARBON NaHCO$_3$	RATIO
S			2	120	50	10	12	
S			7	201	108	49	94	
S-1	0.15	14	7	270	202	100	75	7.2/5.4/2.6/2
S-3	0.4	21	2	430	307	210	120	7.2/5.2/3.4/2
S-4	0.2	22	2	107	112	42	40	5.4/5.6/2.0/2
			2	122	98	54	42	5.8/4.6/2.6/2
			1	135	100	53	35	7.8/5.8/3.0/2
S-5	0.2	180	3	225	139	90	77	5.8/3.6/2.4/2
S-6	SAT	3	2	508	601	298	197	5.2/6.0/3.0/2
S-7	1.0	30	5	293	277	180	118	5.0/4.6/3.0/2
S-8	SAT	3	3	421	357	245	185	4.6/3.8/2.6/2

Note: Column 2- concentration of oxidizing solution (NH$_4$)$_2$S$_2$O$_8$
Column 3- length of oxidation time
Column 4- Length of time equilibrated with bases.
Column 9- Ratios of the base consumption

Neutralization of Acidic Surface Oxides. The Samples were Outgassed under Vacuum at Different Temperatures for 24 Hrs

SAMPLE	OUTGASSED TEMP. °C	CONC. MOLAR	OXID. DAYS	EQUIL. DAYS	BASES USED, meq/100g.			CARBON	RATIO
					NaOEt	NaOH	Na_2CO_3	$NaHCO_3$	
L-7		0.2	22	2	155	108	49	35	8.8/6.2/2.8/2
	490			2	70	45	15	8	17 /11 /3.6/2
	890			2	36	28	9	6	12 / 9 /3.2/2
L-9		SAT	3	2	322	380	257	187	3.4/4.0/2.8/2
	890			2	36	28	9	6	12 / 9 /3.2/2
L-12		SAT	3	3	310	292	205	150	4.2/3.8/2.7/2
	890			3	65	55	15	10	6.5/5.5/1.5/1
S-3		0.4	21	2	430	307	210	120	7.2/5.2/3.4/2
	200			2	450	295	185	132	7.8/4.4/2.8/2
	490			2	132	108	57	29	9.0/7.4/2.8/2
S-6		SAT	3	2	508	601	298	197	5.2/6.0/3.0/2
	600			2	102	66	23	16	13 /8.4/3.0/2
	890			2	53	50	21	11	9.8/9.2/3.8/2
S-8		SAT	3	3	421	357	245	185	4.6/3.8/2.6/2
	890			3	60	60	25	20	6.0/6.0/2.5/2

TABLE III.

TABLE IV. SURFACE ACIDITIES AND SURFACE AREAS OF CARBON ADSORBENT SAMPLES

SAMPLE	BASE CONSUMPTION, Meq/100g				SURFACE GROUPS, meq/100g.				BET(N_2) m^2/g
	NaOEt	NaOH	Na_2CO_3	$NaHCO_3$	IV	III	II	I	
LC325	59	48	28	30	11	20	--	30	1076
LC325 O*	310	292	205	150	18	87	55	150	861
LC325 OR	246	210	129	92	36	81	36	92	840
LC325 OD	65	55	15	10	10	40	5	10	1015
S51	108	71	48	40	37	23	8	40	586
S51 O*	421	357	245	185	64	112	60	185	596
S51 OR	215	181	112	80	34	70	32	80	836
S51 OD	60	60	25	20	--	35	5	20	725
P607	265	203	132	109	62	71	23	109	646
P607 O	350	267	185	152	83	82	33	152	613
P607 OR	298	223	142	107	75	81	35	107	640

Note: The oxidized LC325 used here was the L-]2, and the oxidized S5] was the S-8.
All the samples in this table are different from samples described in Table I, II and III.

TABLE V. PLATEAU VALUES FOR THE ADSORPTION OF PHENOL & BENZENESULFONATE

SAMPLE	BENZENESULFONATE,70 mol/l. moles/g	moles/m^2	PHENOL, 250 mol/l. moles/g	moles/m^2	SURFACE AREA BET (N$_2$) m^2/g
P607	100	0.155			646
P607 O	33	0.054			613
P607 OR	64	0.100			640
LC325	229	0.213	1230	1.143	1076
LC325 O[1]	20	0.023	460	0.534	861
LC325 OR	89	0.106	540	0.642	840
LC325 OD			1160	1.142	1015
S51	195	0.333	775	1.322	586
S51 O[2]	13	0.022	275	0.461	596
S51 OR	26	0.031	530	0.634	836
S51 OD			1090	1.507	725

1-same as L-]2;
2-same às S-8

TABLE **VI**. PERCENTAGE OF ADSORBENT SURFACE AREA (B.E.T.,N_2) OCCUPIED BY BENZENESULFONATE AND BY PHENOL

SAMPLE	% OF SURFACE OCCUPIED BY BENZENESULFONATE	% OF SURFACE OCCUPIED BY PHENOL	TOTAL ACIDITY
P607	2.08		265
P607 O	0.73		350
P607 OR	0.13		298
LC325	2.86	28.35	59
LC325 O	0.31	13.24	310
LC325 OR	1.42	15.92	246
LC325 OD		28.40	65
S51	4.48	32.78	108
S51 O	0.30	11.43	421
S51 OR	0.42	15.72	215
S51 OD		37.40	60

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TABLE VII. SURFACE AREAS FROM THE LANGMUIR PLOT (PHENOL ISOTHERMS)

CONCENTRATION RANGE	SAMPLES	SLOPE	X_m $\mu mol/mg$	SURFACE AREA*, M^2/G $\Phi=18$ A2	$\Phi=41.2$ A2
above 70 μmole/l.	LC325	0.636	1.571	170	
	LC325 O	1.460	0.686	74.4	
	LC325 OR	1.333	0.750	81.3	
below 70 μmole/l.	LC325	1.08	0.927		230
	LC325 O	2.90	0.345		85.6
	LC325 OR	2.81	0.356		88.3
above 120 μmol/l.	S51	0.942	1.061	115	
	S51 O	2.86	0.350	37.9	
	S51 OR	1.357	0.736	79.8	
	S51 OD	0.688	1.452	157.3	
below 120 μmol/l.	S51	1.56	0.643		159
	S51 O	5.56	0.180		44.6
	S51 OR	2.60	0.385		95.5
	S51 OD	1.06	0.940		233

Note: Surface areas are used on X_m, not on BET N_2 adsorption
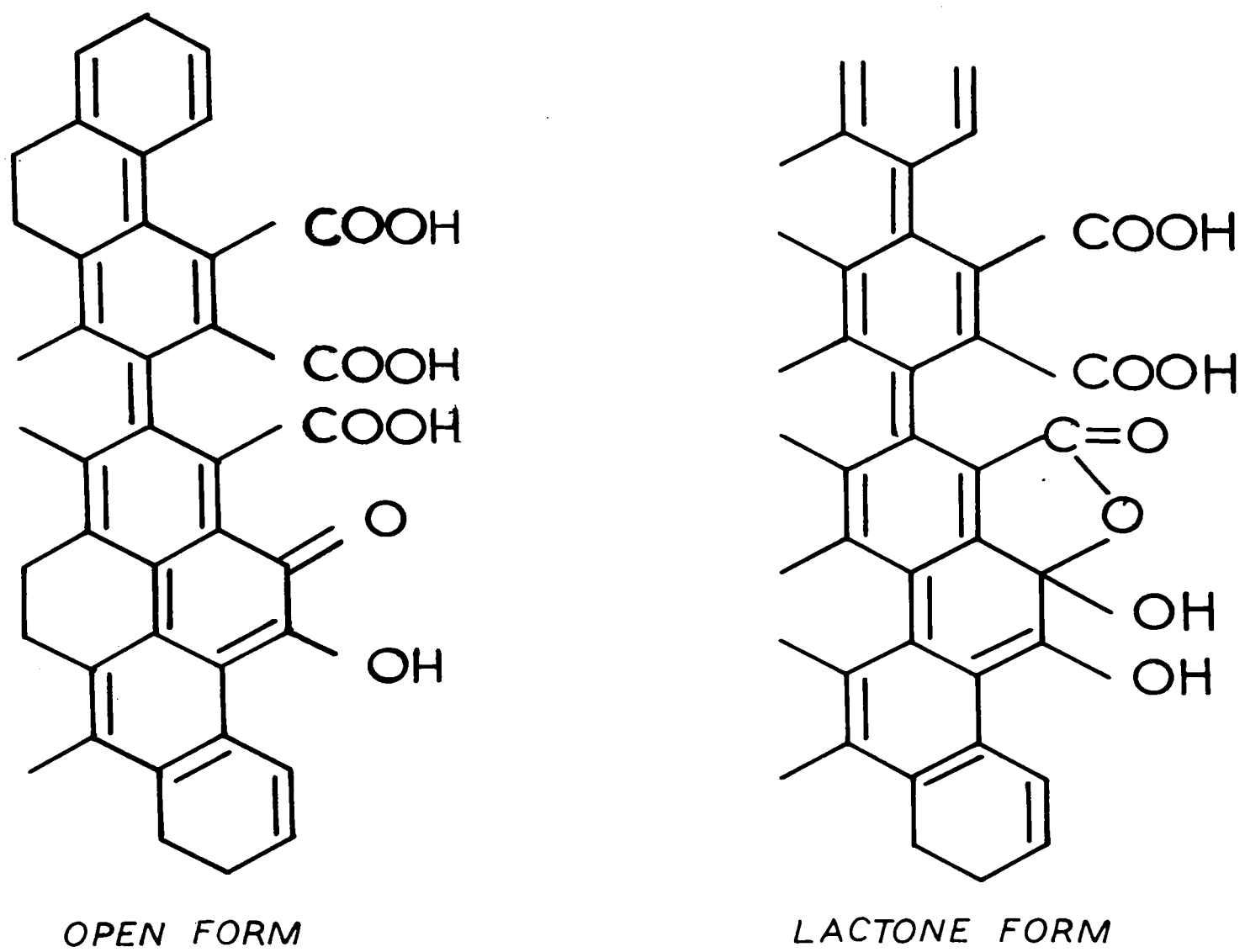
41

OPEN FORM

LACTONE FORM

FIGURE 1   POSSIBLE STRUCTURES OF CARBON SURFACE OXIDES

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Figure 2

Rates of Adsorption of Phenol on Activated Carbon "Columbia LC325" in Aqueous Solution at 30°C C_0=0.4 mmoles/liter
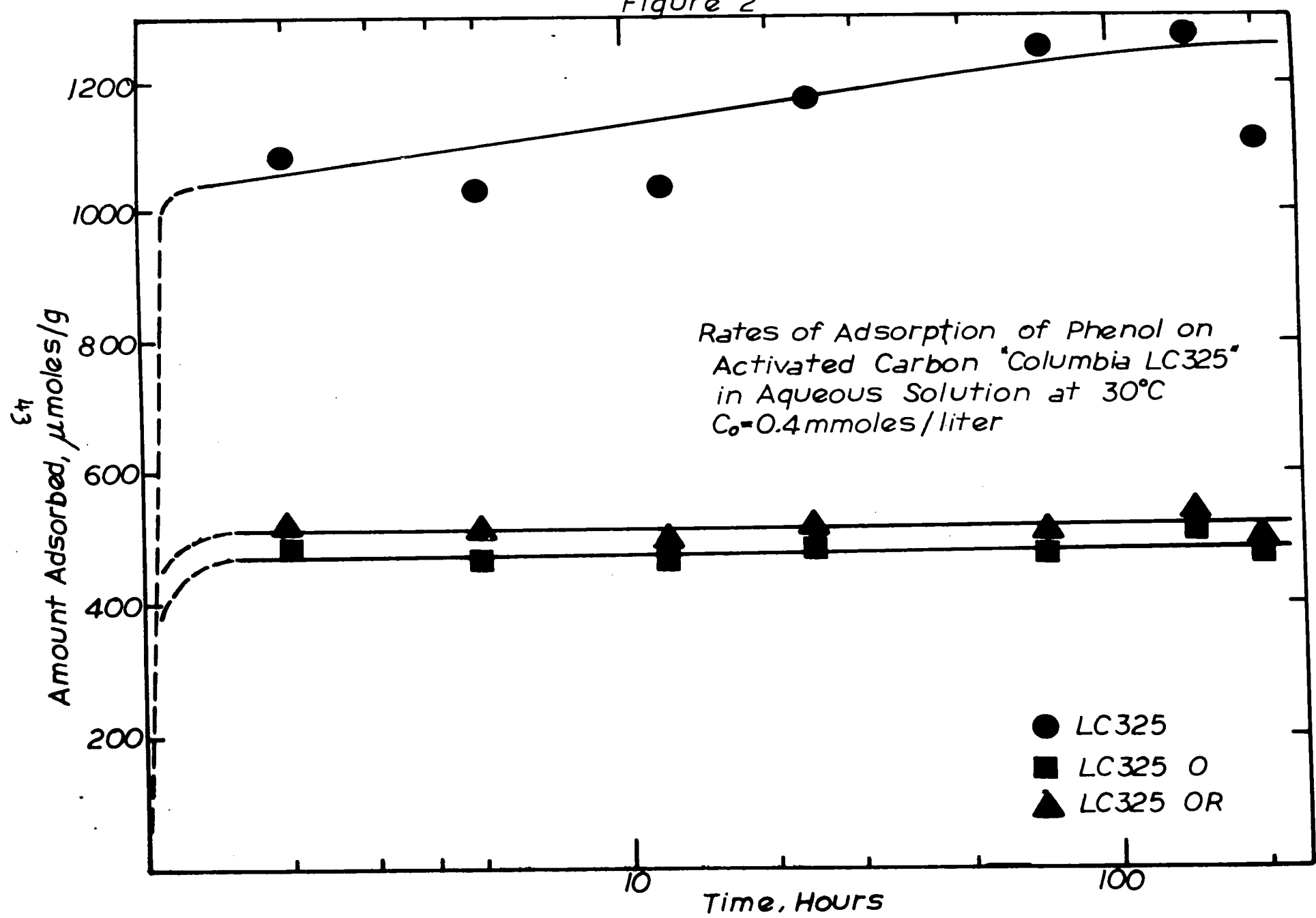
Fig. 3   Rates of Adsorption of Phenol by Activated Carbon "Darco S51"
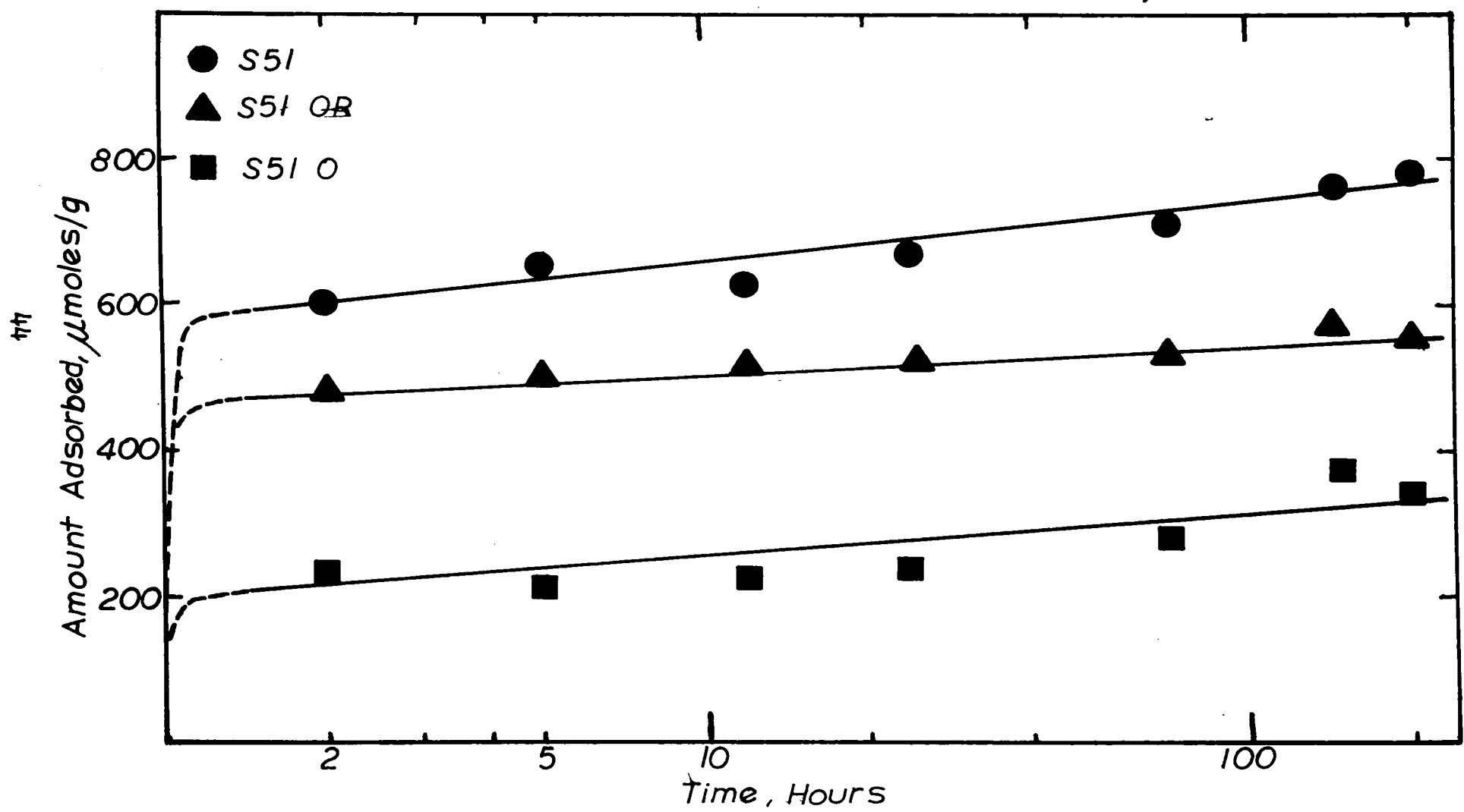in Aqueous Solution, 30°C, C_o=0.4mmoles/l.

Fig. 4 Rates of Adsorption of Sodium Benzene Sulfonate on Activated Carbon
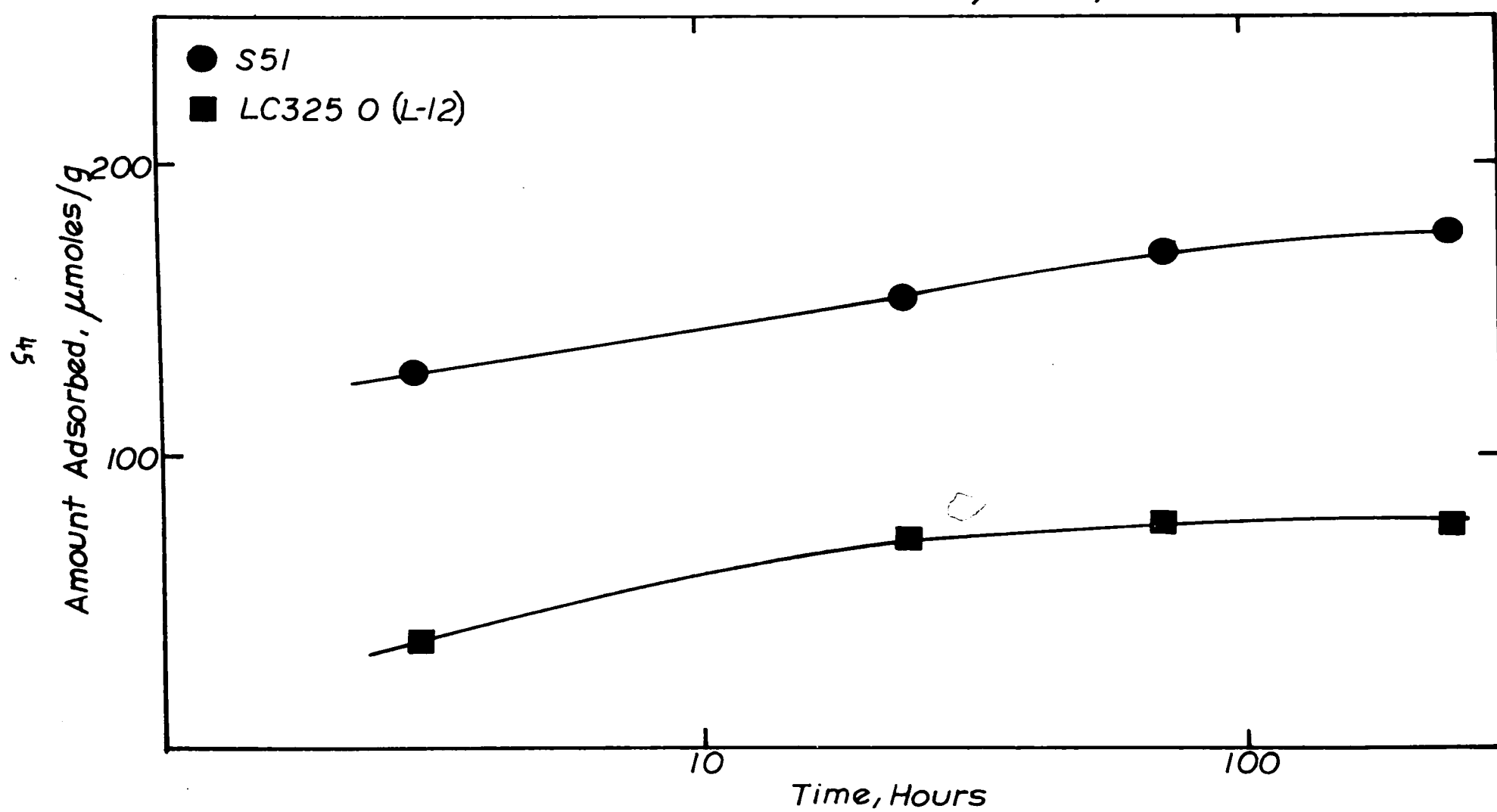in Aqueous Solution, 30°C, $C_0 = 40\mu moles/l$.

Fig. 5   Adsorption Isotherms of Phenol on Activated Carbon "Columbia LC325" in Aqueous Solution, 30°C, 3 Days Equilibrium Time

Fig. 6 Adsorption Isotherms of Phenol on Activated Carbon "Darco S51" in Aqueous Solution 30°C 3 Days Equilibrium Time

Fig. 7   Adsorption Isotherms of Phenol on Activated Carbon "Columbia LC325" in Aqueous Solution 30 C 3 Days Equilibrium Time
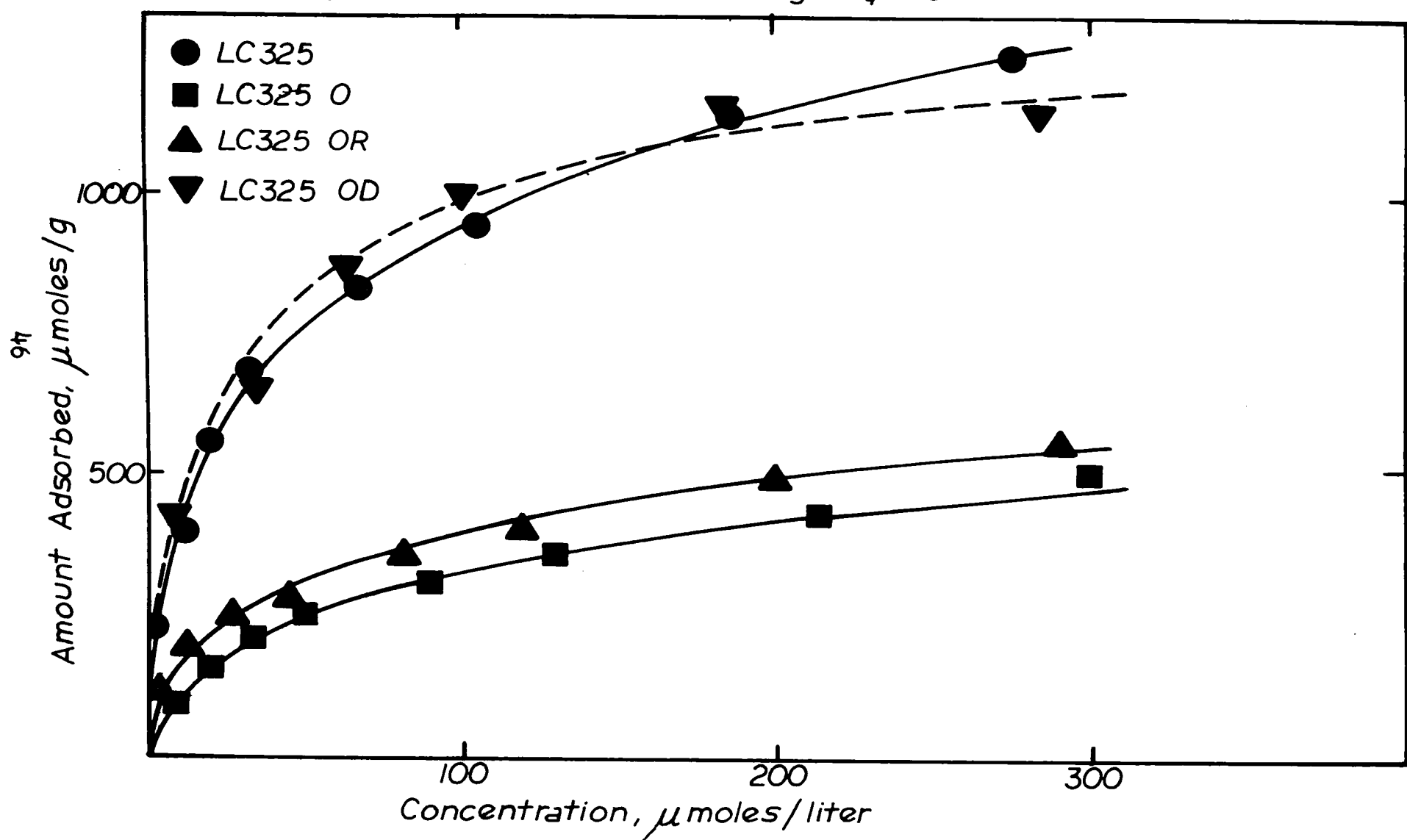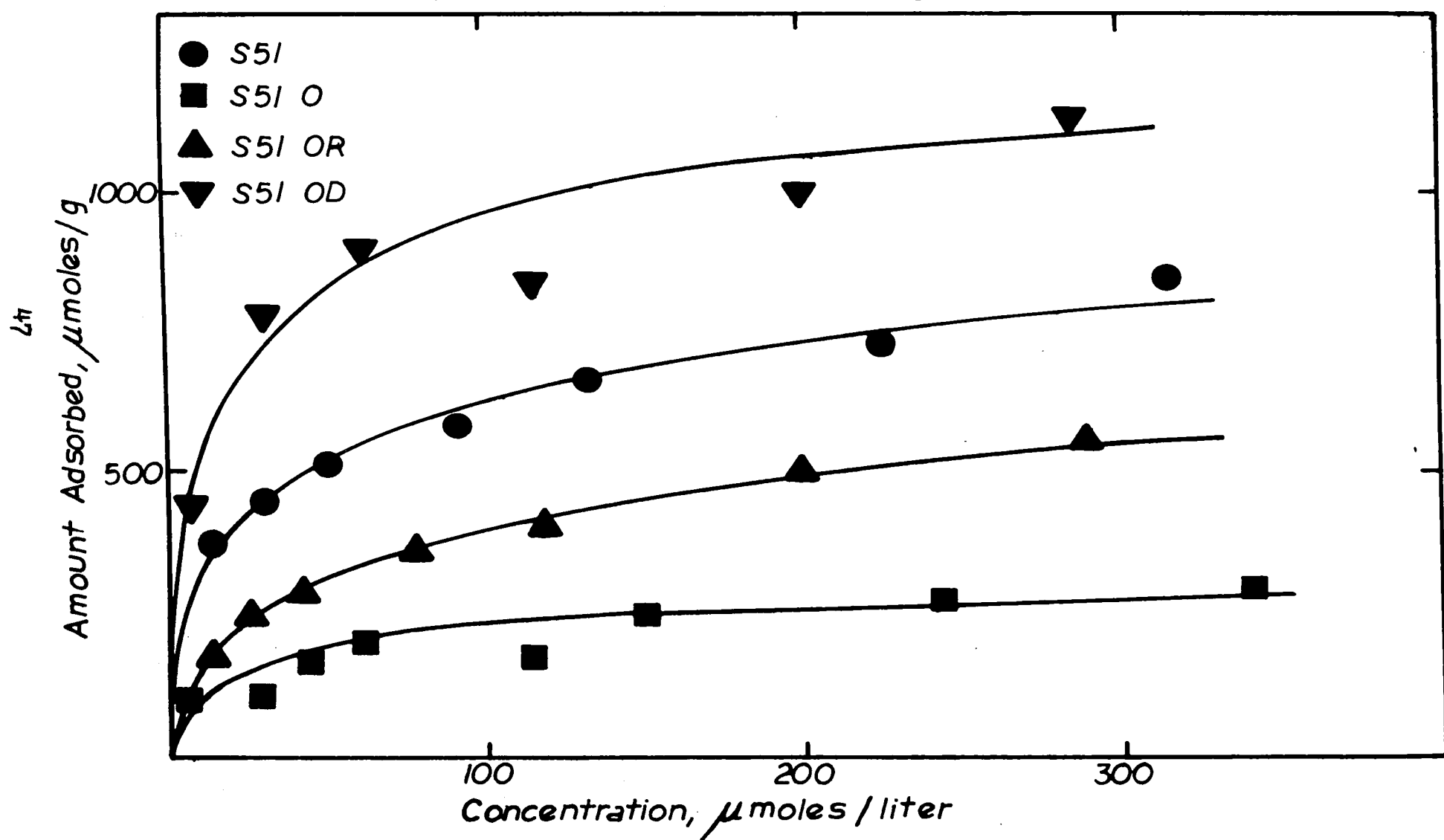
Fig.8   Adsorption Isotherms of Phenol on Activated Carbon "Darco S51" in Aqueous Solution, 30°C, 3 Days Equilibrium Time
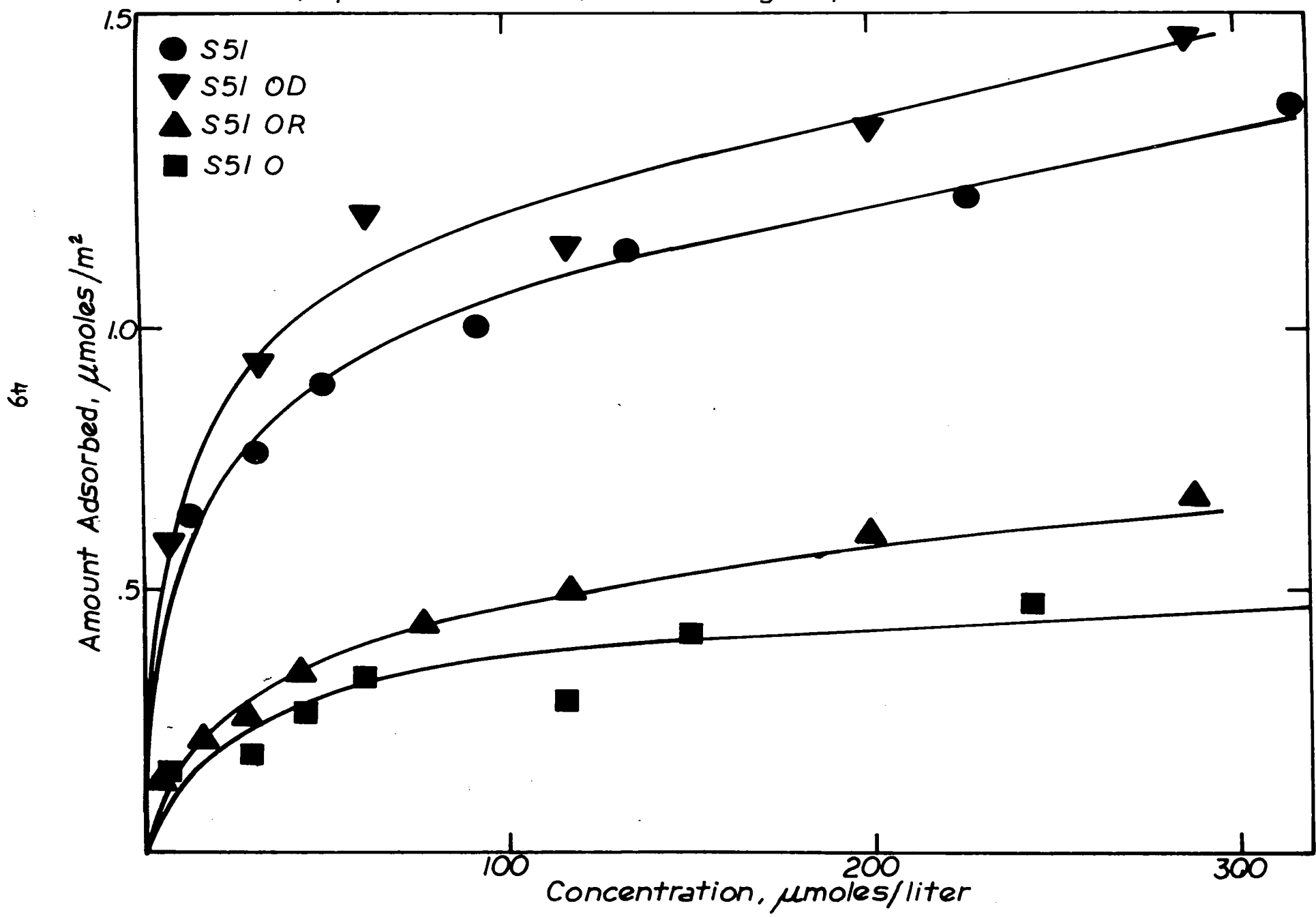
Fig. 9 Adsorption Isotherms of Phenol on Carbon Black "Black Pearl P607"
in Aqueous Solution, 30°C , 3 Days Equilibrium Time
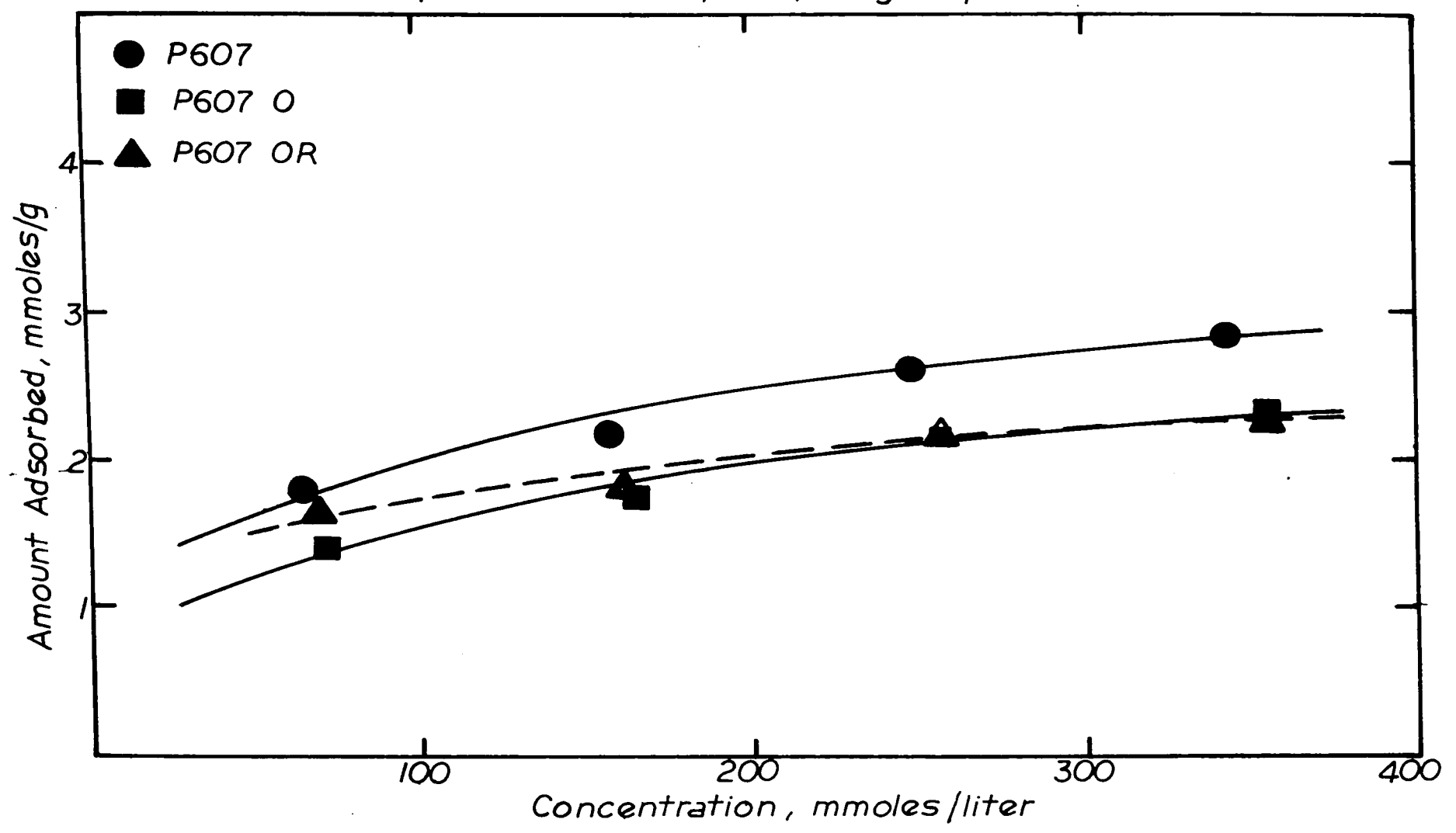
Fig. 10 Adsorption Isotherms of Phenol on Activated Carbon "Columbia LC325" in Aqueous Solution 30 C 3 Days Equilibrium Time
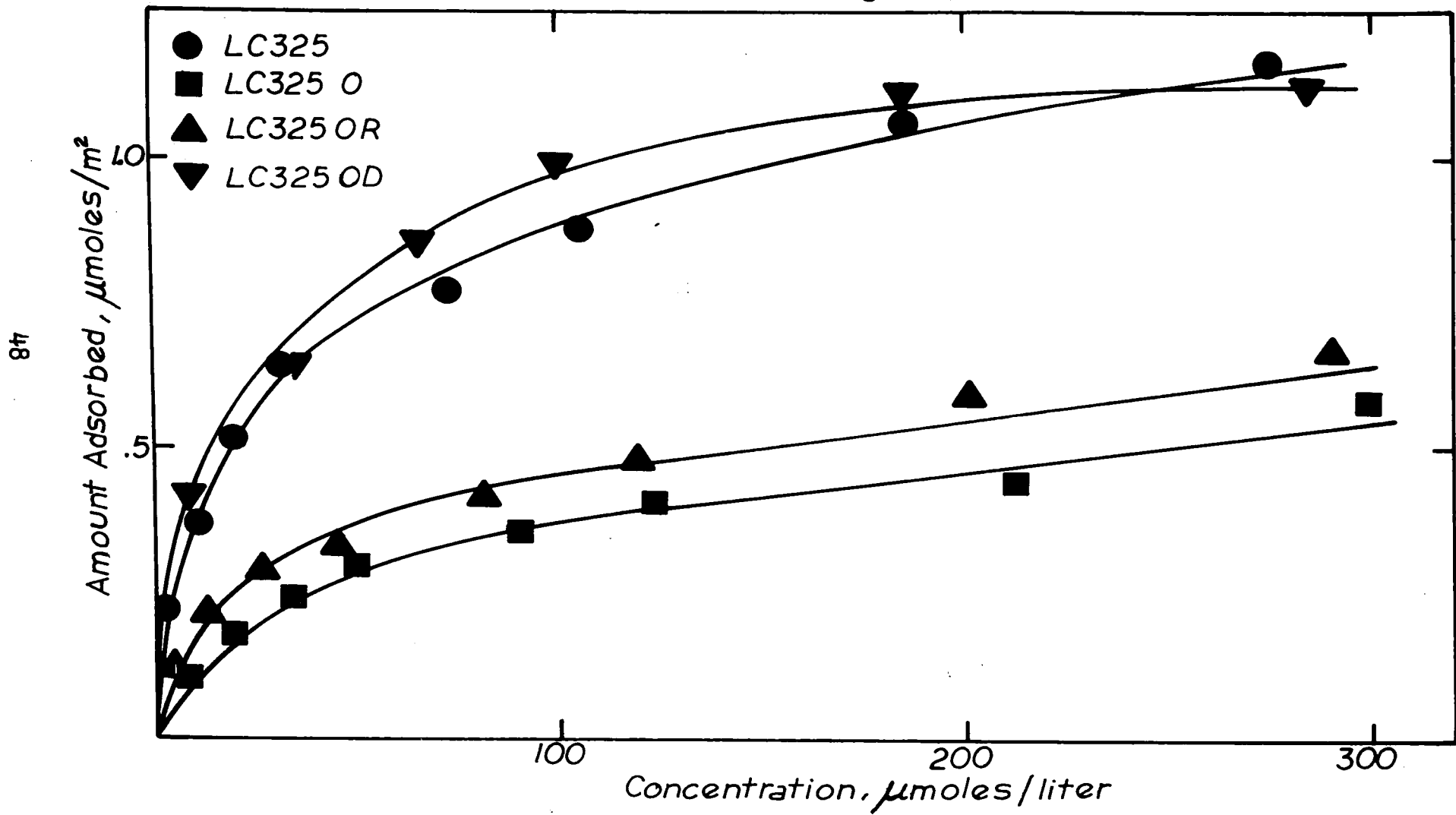
51
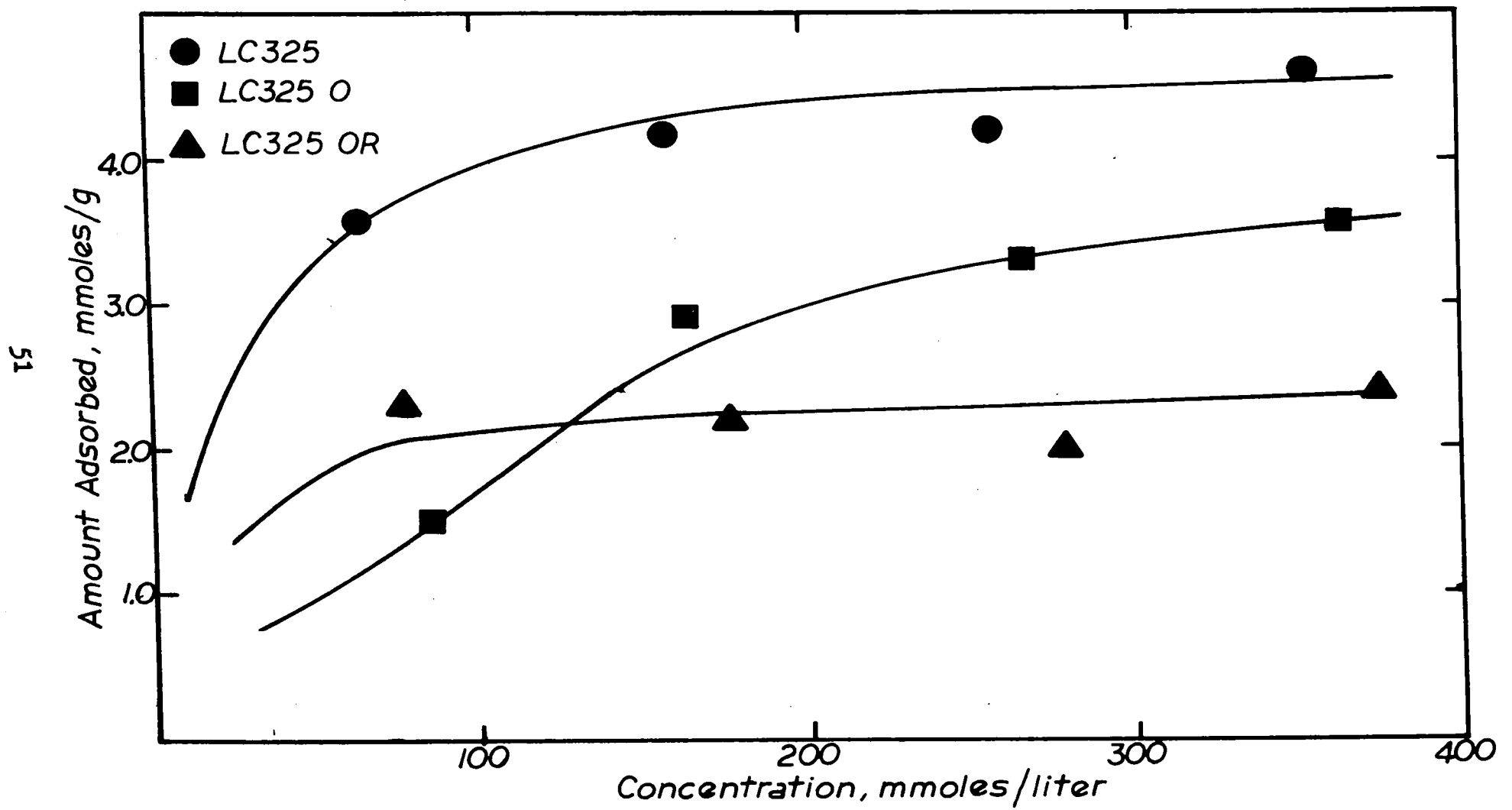
Fig. 11   Langmuir Plots of Adsorption Isotherms for Phenol (30°C)
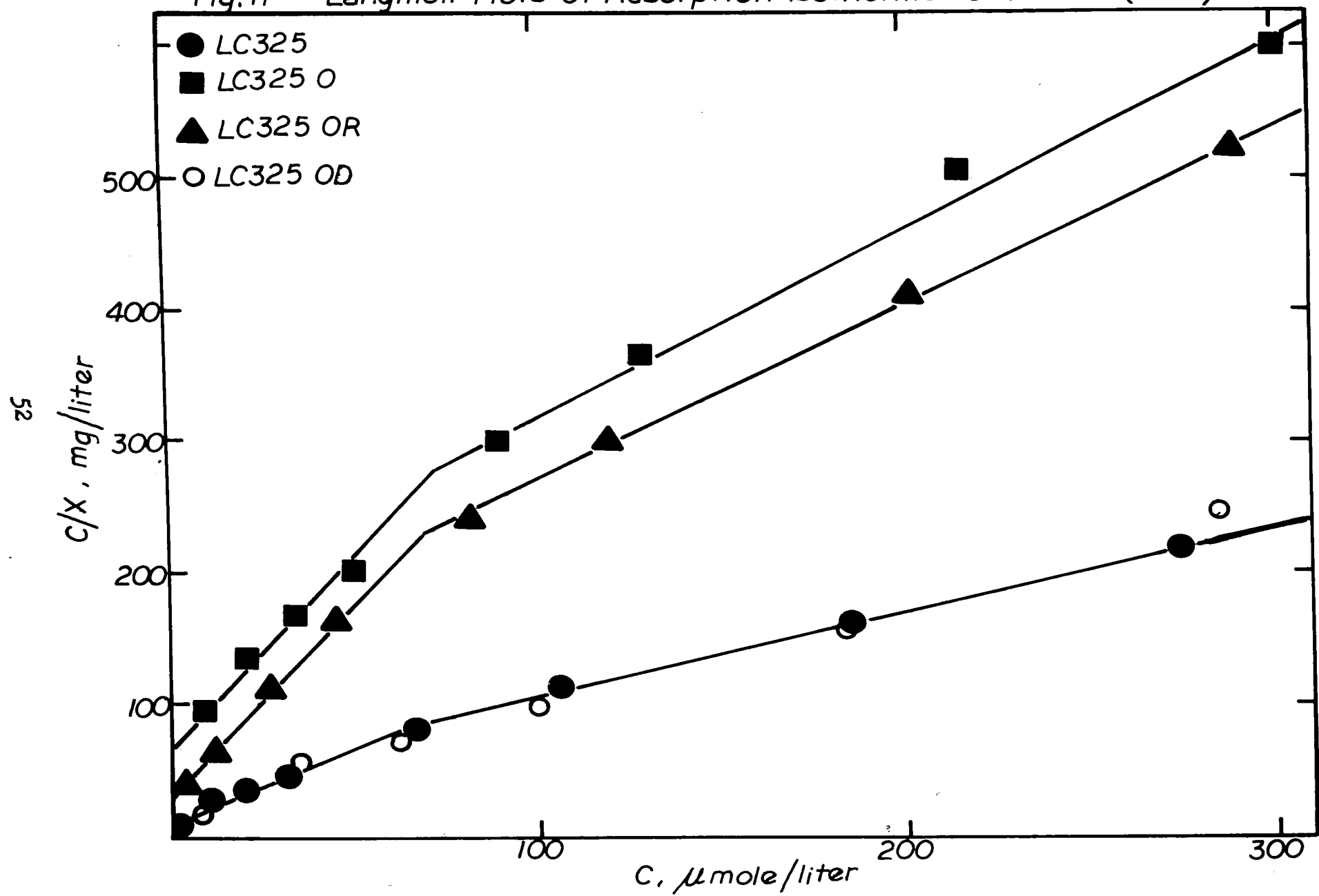
Fig. 12   Langmuir Plots of Adsorption Isotherms for Phenol (30°C)
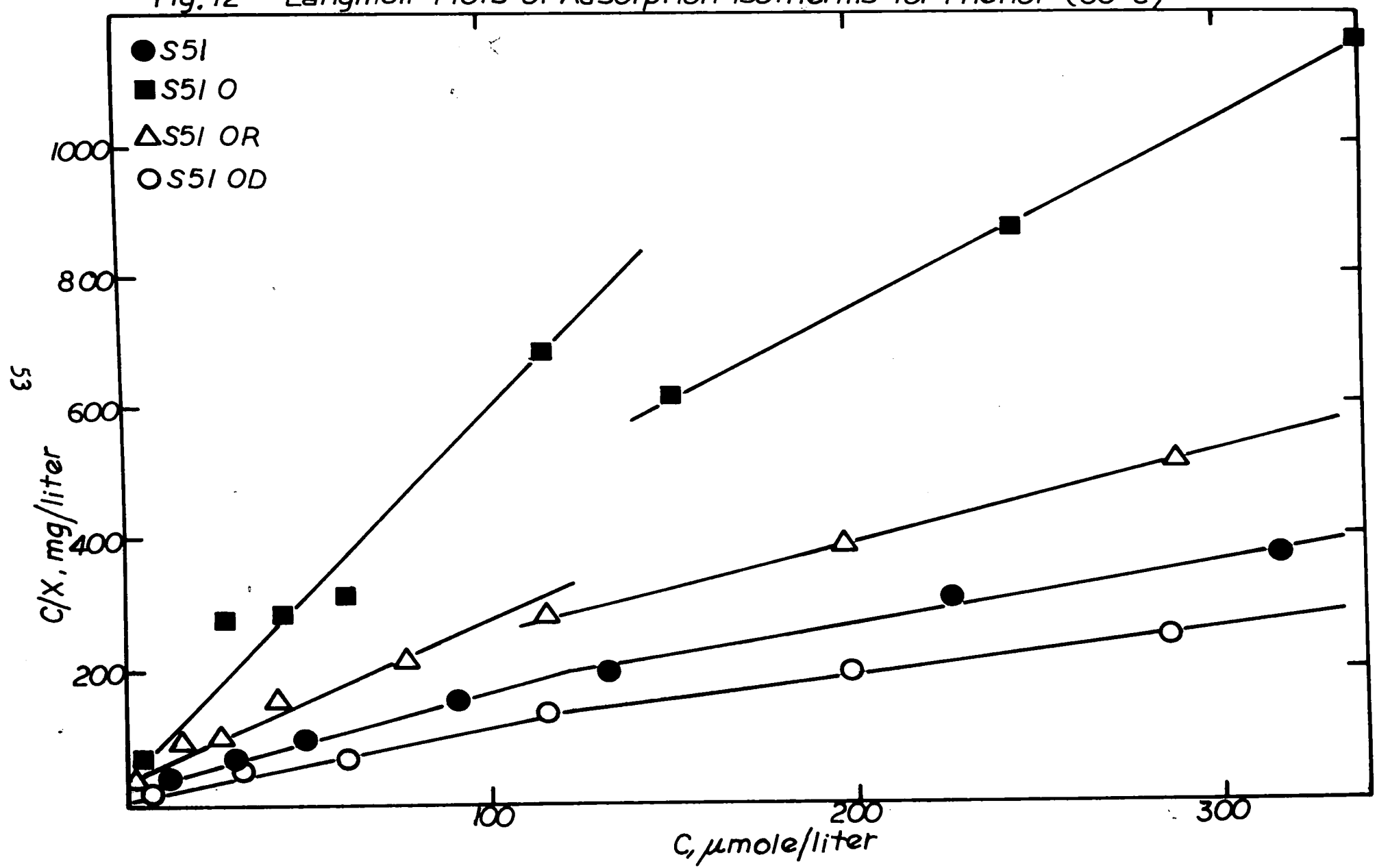
53

Adsorption Isotherms of Sodium Benzene Sulfonate on Activated Carbon "Columbia LC325" in Aqueous Solution, 30°C, 3 Days Equilibrium Time
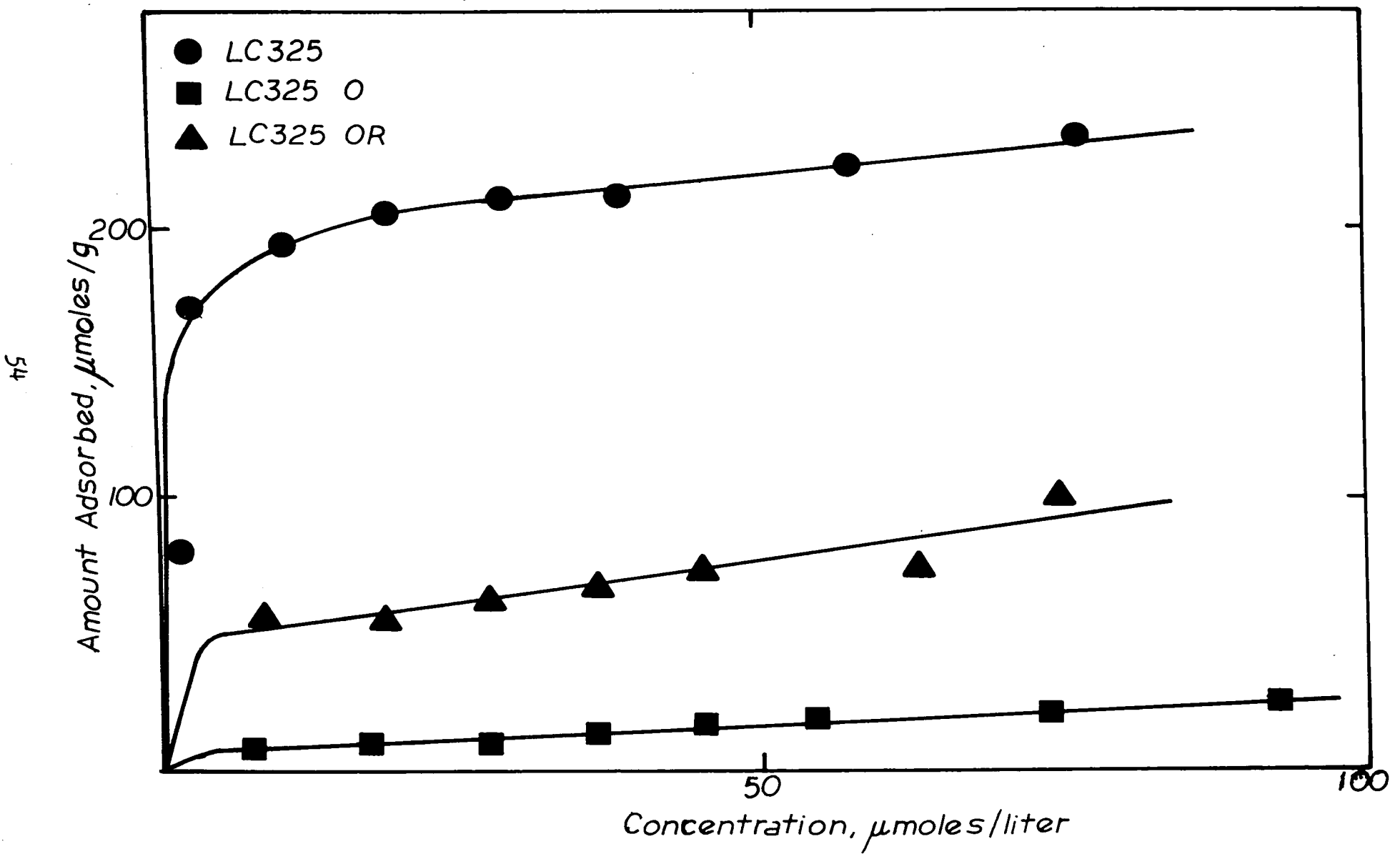
Figure 13

Adsorption Isotherms of Sodium Benzene Sulfonate on Activated Carbon "Darco S51" in Aqueous Solution, 30°C, 3 Days Equilibrium Time
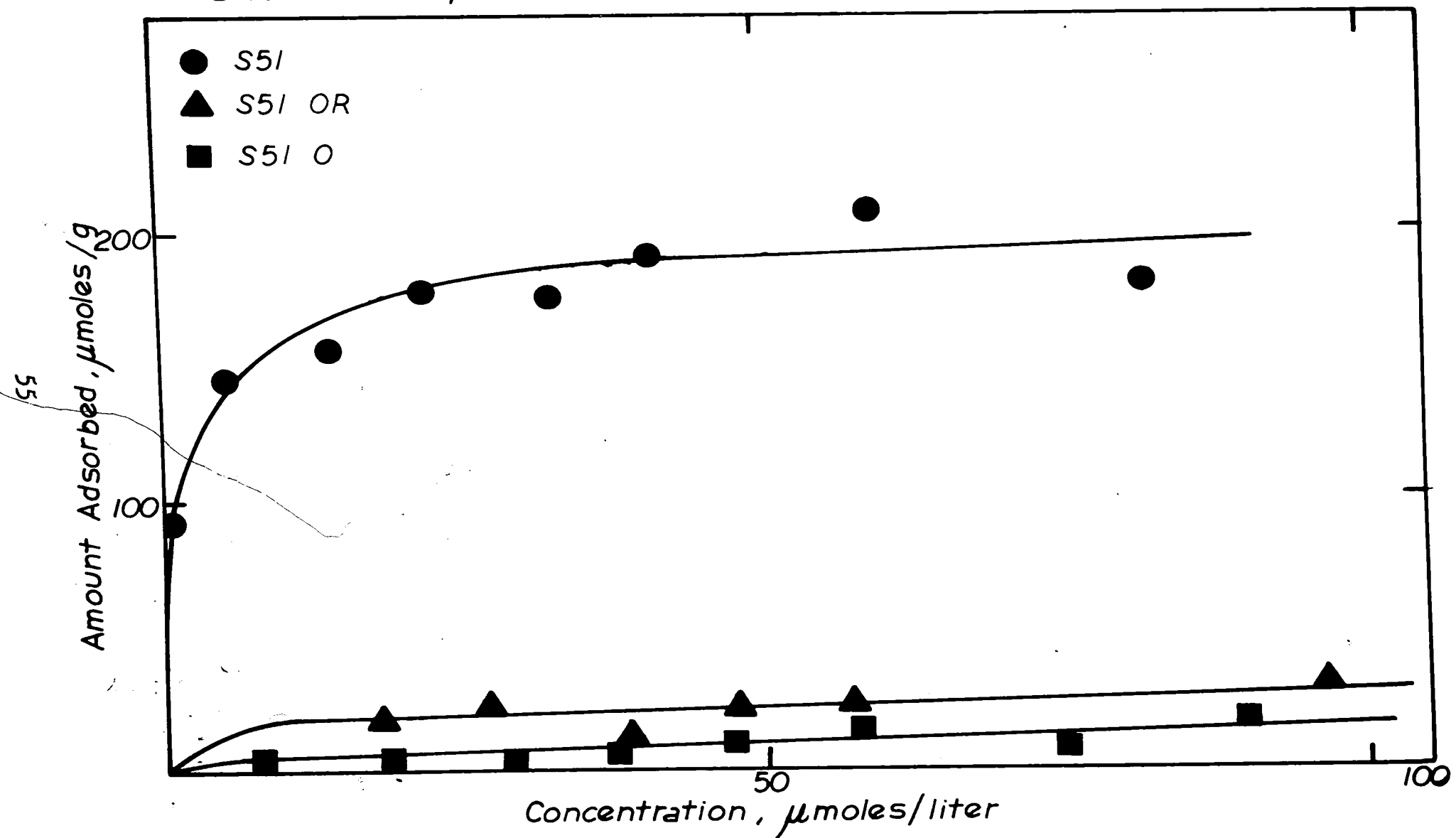
Figure 14

Adsorption Isotherms of Sodium Benzene Sulfonate on Carbon Black
"Black Pearl P607" in Aqueous Solution, 30°C, 3 Days Equilibrium Time
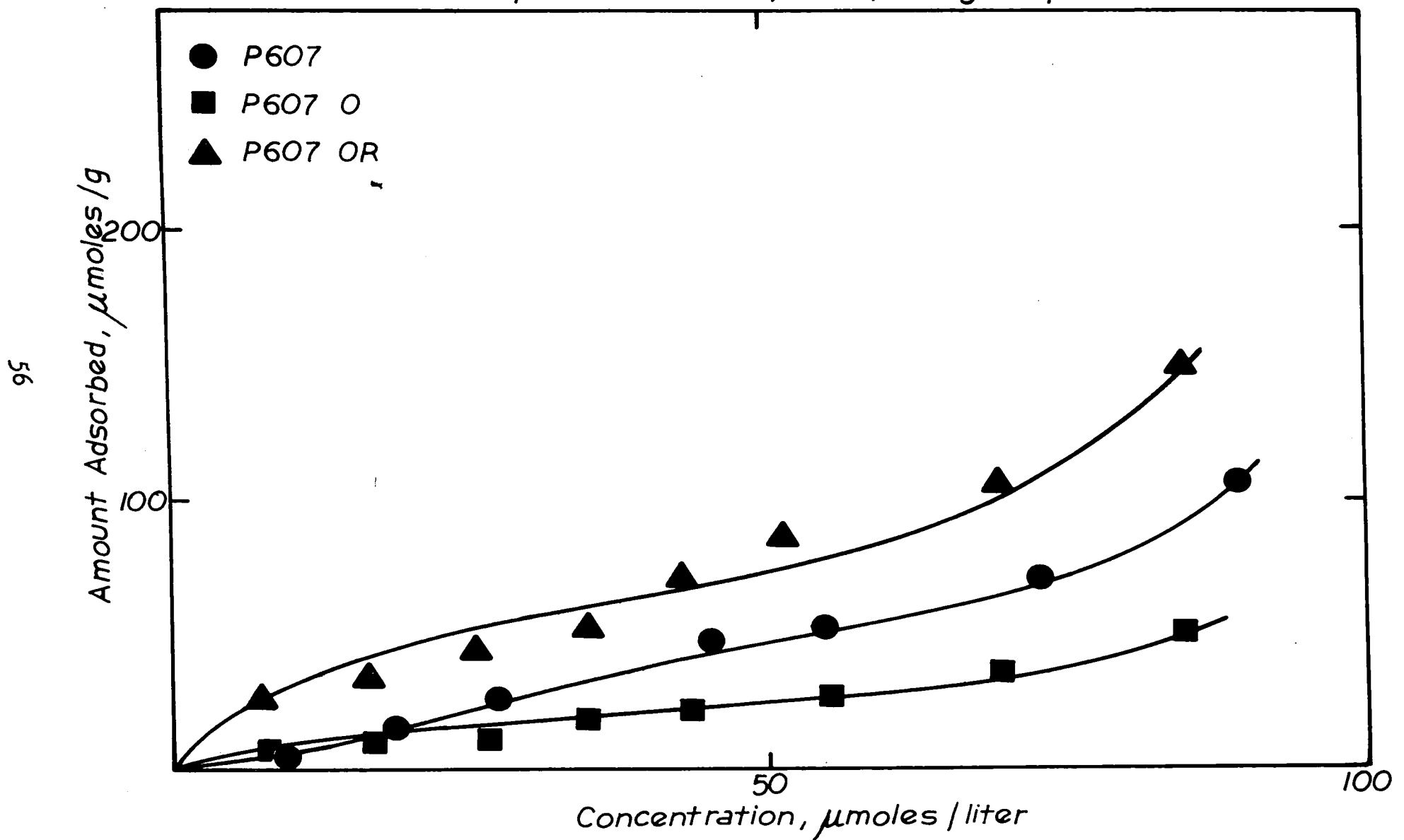
Figure 15

Effect of Ca++ on the Adsortion of Sodium Benzene Sulfonate on Activated
Carbon "Columbia LC325" in Aqueous Solution, 30°C, 3 Days Equil. Time
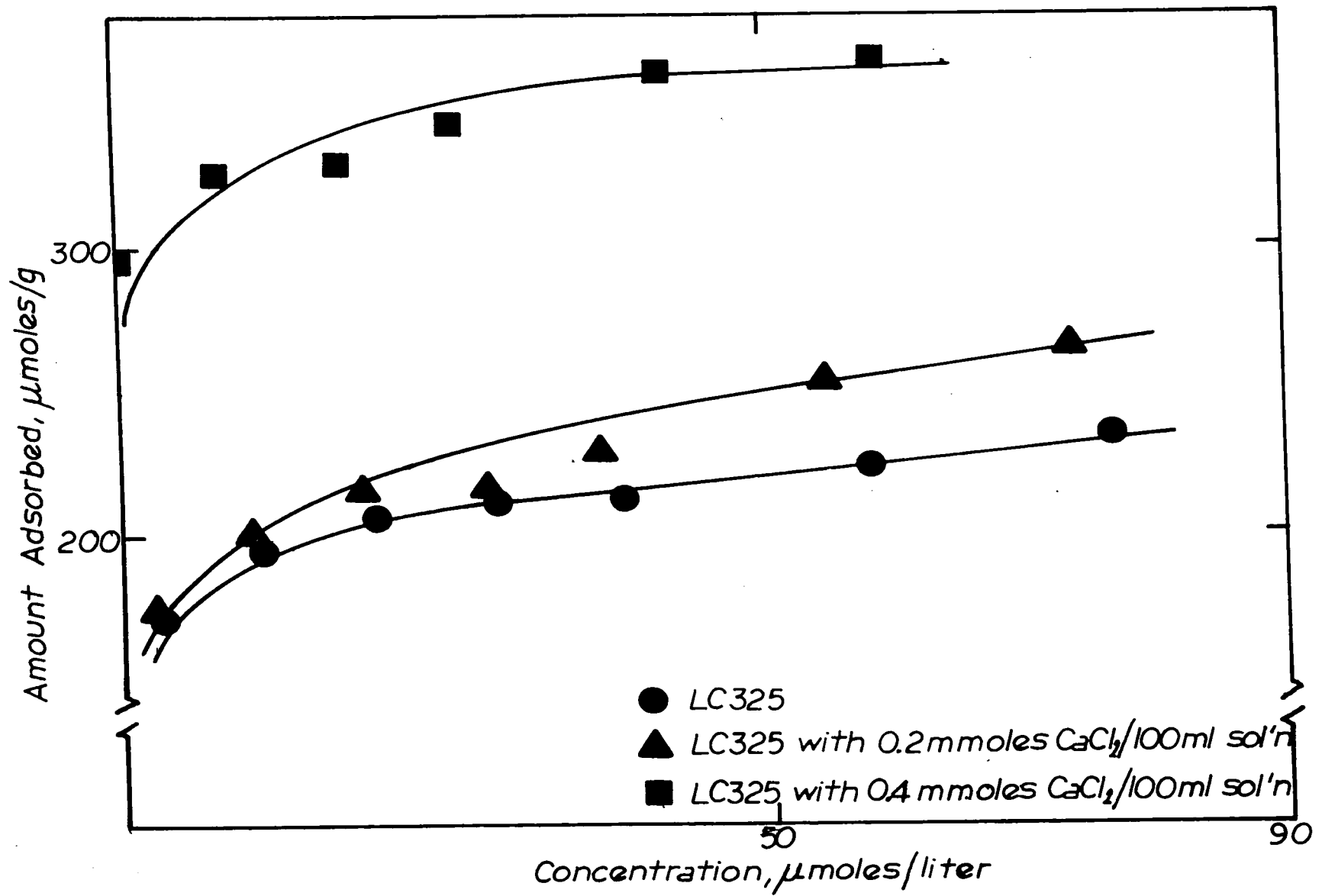
Figure 16

Effect of Ca⁺⁺ on the Adsorption of Sodium Benzene Sulfonate on Activated Carbon "Darco S51" in Aqueous Solution, 30°C, 3 Days Equilibrium Time
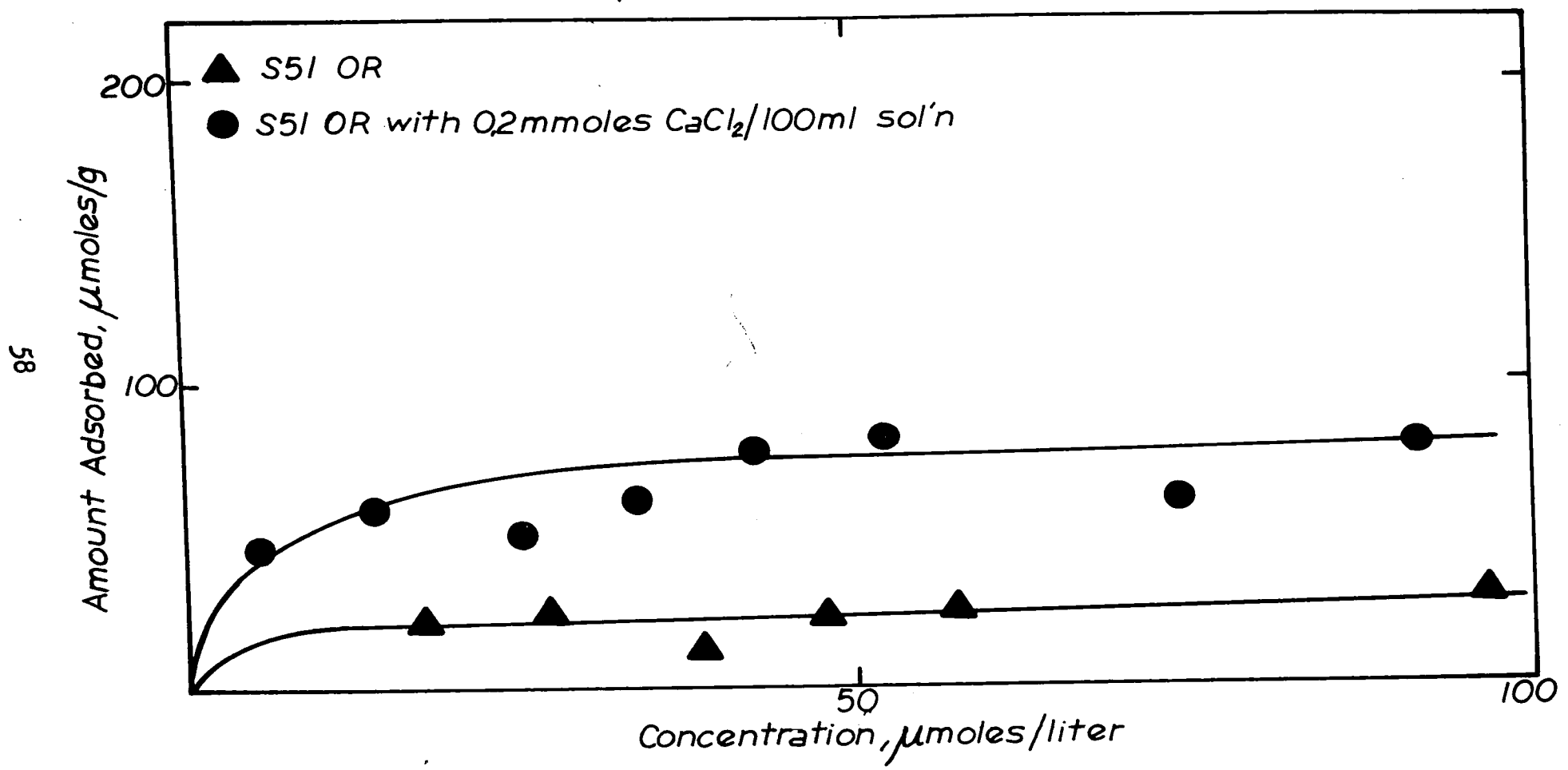
Figure 17

Effect of Ca⁺⁺ on the Adsorption of Sodium Benzene Sulfonate on Carbon Black "Black Pearl P607" in Aqueous Solution, 30°C, 3 Days Equilibrium Time
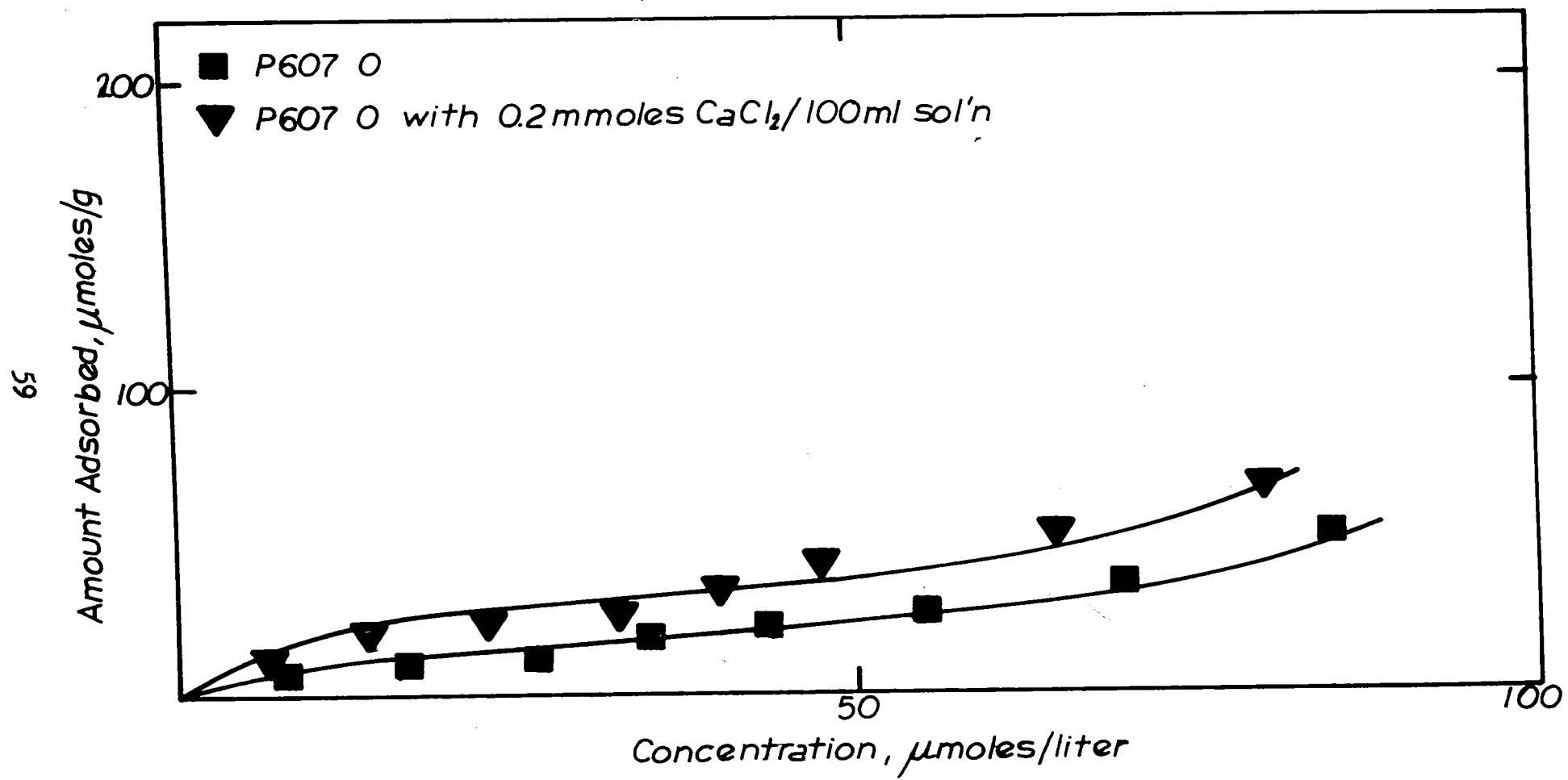
Figure 18

Effect of Ca on the Adsorption of Phenol on Activated Carbon "Columbia LC325" in Aqueous Solution, 30°C, 3 Days Equilibrium Time
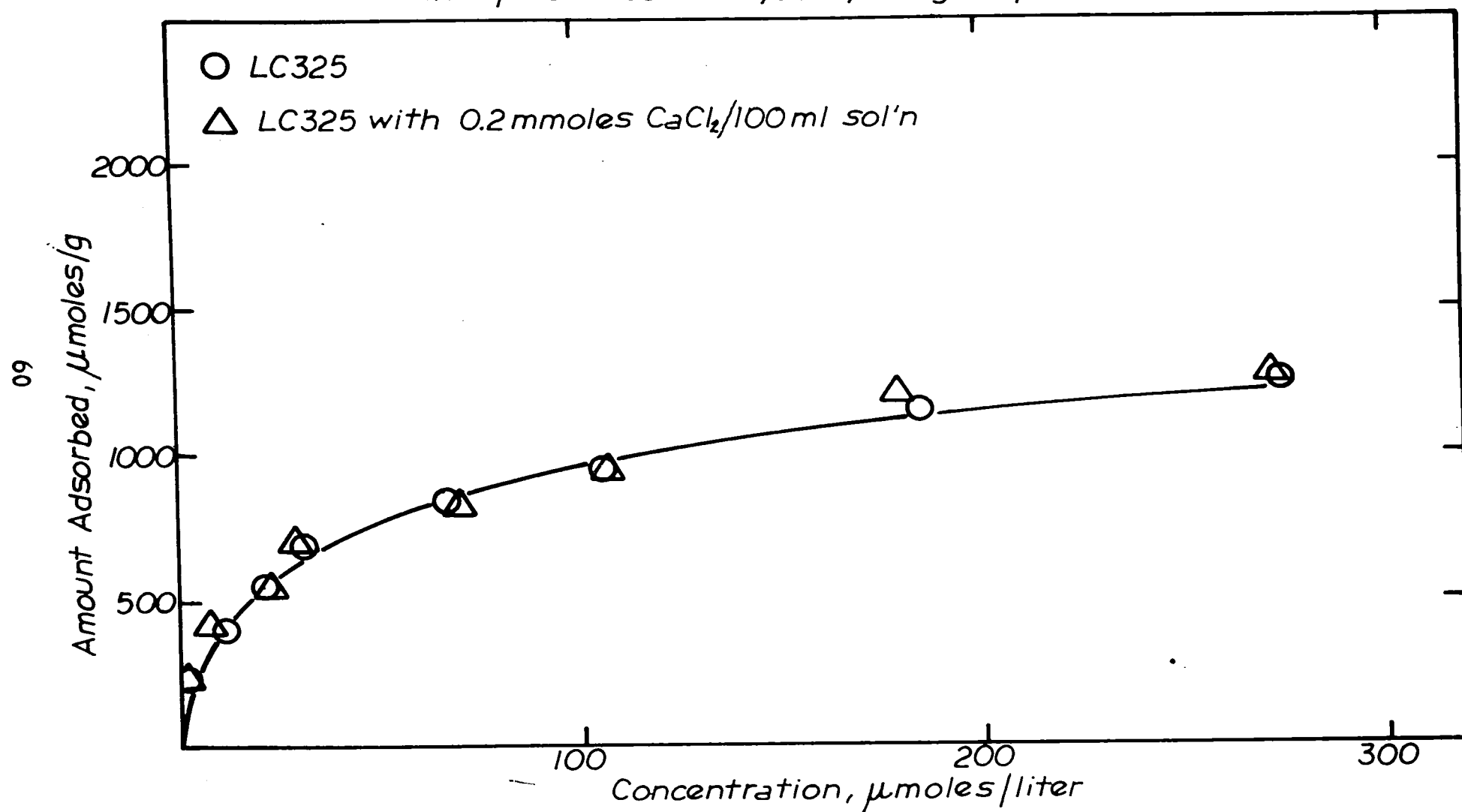
Figure 19

Total Acidity vs. % Area Covered by Phenol

- ● LC325
- ▲ S51
- ▢ LC325 Ezra's data

Figure 20

Total Acidity vs % Area Covered by Benzenesulfonate

● LC325
▲ S51
■ P607

% Area Covered

Total Acidity, meq/100g
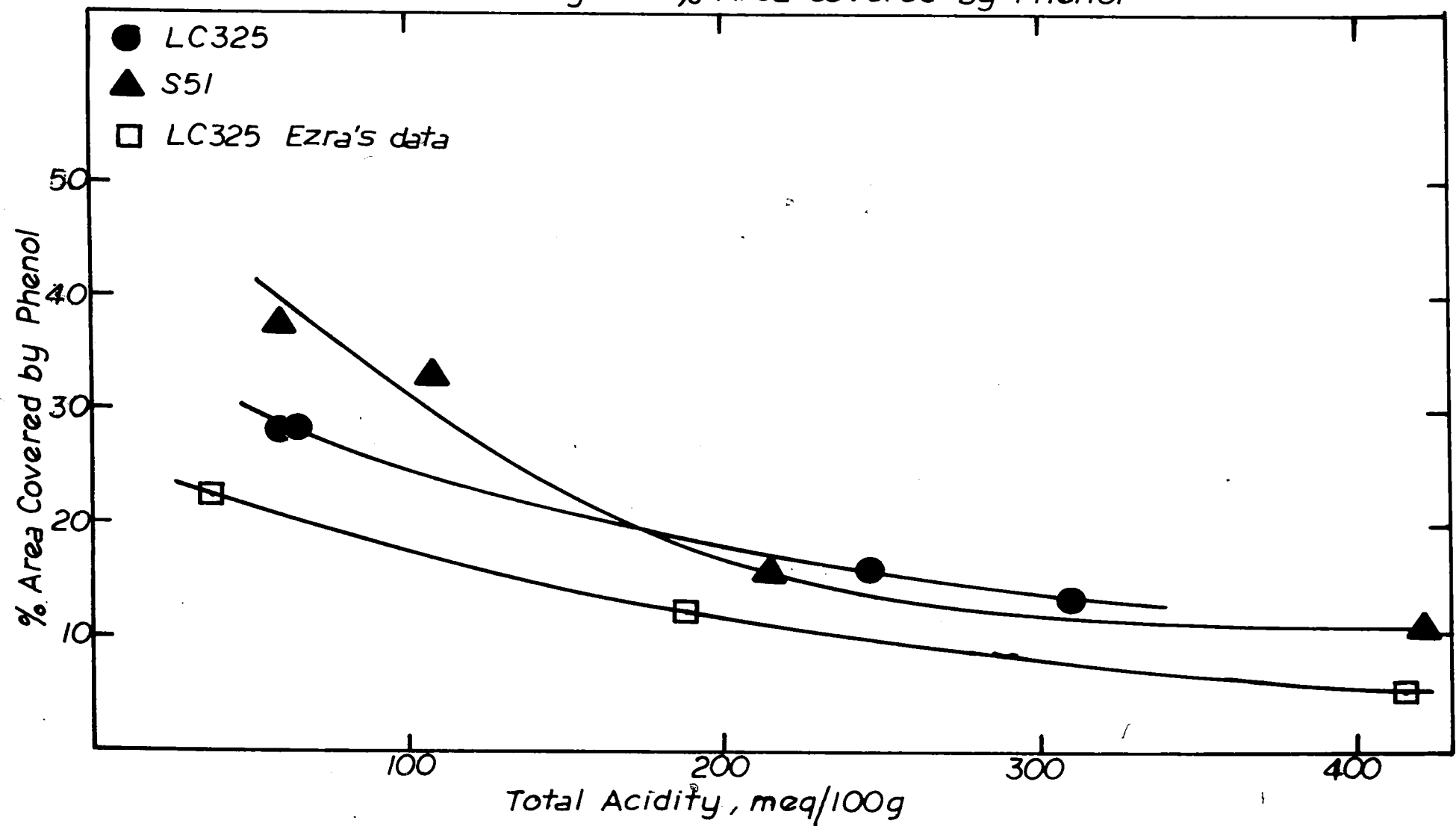
Figure 21

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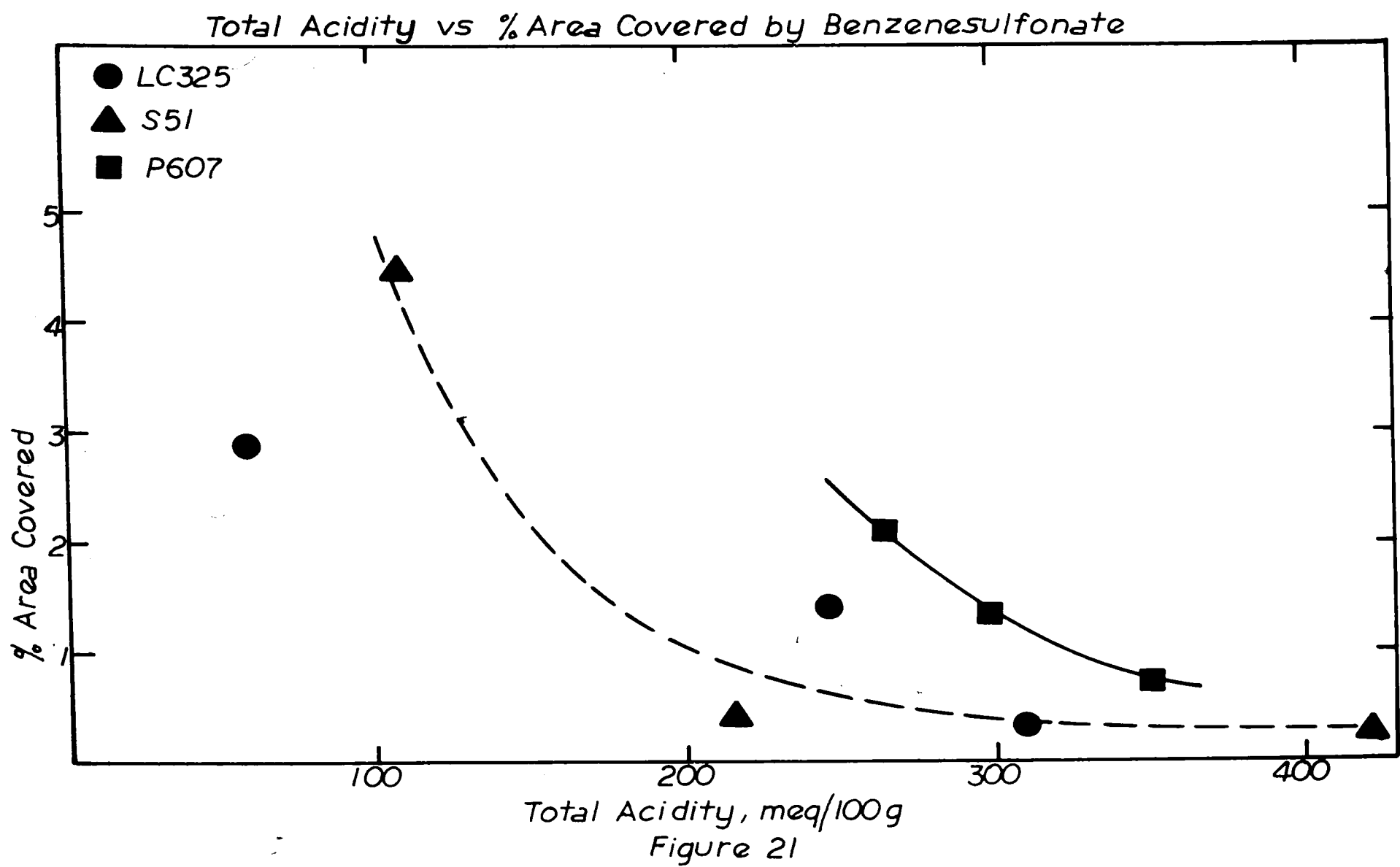
ADSORPTION OF PHENOL ON LC325

	C, μmol/l.	X, μmol/g	X' μmol/m^2	C/X, mg/l.
	275	1,250	1.162	220
	186	1,140	1.060	163.0
	106	940	0.870	112.8
LC325	67	830	0.772	80.7
	32	680	0.632	47.0
	20	550	0.511	36.4
	11	390	0.363	28.2
	2	230	0.214	8.7
	300	500	0.581	600
	215	425	0.434	506
	129	352	0.409	367
LC325 O	90	300	0.349	300
	50	250	0.290	200
	34	205	0.238	166
	20	150	0.174	133
	8	85	0.099	94
	289	555	0.660	521
	202	490	0.583	412
	120	400	0.476	300
LC325 OR	82	340	0.405	241
	45	275	0.327	164
	27	240	0.286	112
	12	190	0.214	63
	4	105	0.125	38
	285	1,150	1.133	248
	184	1,160	1.142	158
LC325 OD	100	1,000	0.985	100
	63	870	0.857	72.4
	35	650	0.640	54
	8	420	0.414	19

Note: 0.050 g. of LC325 & LC325 OD in 500 ml. solution
0.100 g. of LC325 O & LC325 OR in 500 ml. solution.
Conditions: 30°C, 3 days equilibrium time

ADSORPTION OF PHENOL ON S51

	C, μmol/l.	X, μmol/g	X' μmol/m^2	C/X, mg/l.
	316	840	1.433	376
	228	730	1.245	311
	133	670	1.143	198
S51	92	580	0.989	158
	49	510	0.870	96
	31	440	0.751	70.5
	13	370	0.631	35.0
	-	250	0.427	--
	341	296	0.495	1156
	244	280	0.470	871
	151	245	0.411	616
S51 O	116	170	0.285	682
	61	195	0.327	312
	44	155	0.260	284
	29	105	0.176	276
	6	95	0.159	63
	288	560	0.670	514
	199	505	0.604	394
	118	410	0.490	288
S51 OR	78	360	0.430	216
	43	285	0.341	151
	26	245	0.293	106
	16	170	0.203	94
	3	110	0.132	27
	287	1,130	1.560	254
	200	1,000	1.380	200
S51 OD	117	830	1.145	141
	62	880	1.213	70.5
	32	680	0.939	47
	8	420	0.580	19

Note: S51, S51 OD -   0.050 g. in 500 ml. solution
S51 O & S51 OR - 0.100 g. in 500 ml. solution
Conditions: 30°C, 3 days equilibrium time

ADSORPTION OF BENZENESULFONATE ON LC325

LC325 $\frac{\mu mole}{liter}$	LC325 $\frac{\mu mole}{g.}$	LC325 O $\frac{\mu mole}{liter}$	LC325 O $\frac{\mu mole}{g.}$	LC325 OR $\frac{\mu mole}{liter}$	LC325 OR $\frac{\mu mole}{g.}$
76.5	235	92.7	24.3	75.0	100
57.5	223	73.7	21.0	63.2	74
38.8	212	54.5	18.3	45.3	73.5
29.0	210	45.2	16.0	36.6	67.0
19.5	205	36.3	12.3	27.7	61.5
10.7	193	27.4	8.6	19.0	55.0
3.0	170	17.2	9.3	8.6	57.0
2.0	80	7.7	7.6	--	50.0

ADSORPTION OF BENZENESULFONATE ON S51

S51 $\frac{\mu mole}{liter}$	S51 $\frac{\mu mole}{g.}$	S51 O $\frac{\mu mole}{liter}$	S51 O $\frac{\mu mole}{g.}$	S51 OR $\frac{\mu mole}{liter}$	S51 OR $\frac{\mu mole}{g.}$
82.0	180	90.0	17.5	97.0	30
59.3	207	75.0	7.5	57.5	25
41.0	190	58.0	15.5	47.7	23
32.5	175	47.3	10.5	38.7	13
22.2	178	37.6	6.0	27.5	25
14.4	156	28.8	3.0	18.0	20
5.5	145	18.7	3.2		
0.8	92	8.0	3.8		

ADSORPTION OF BENZENESULFONATE ON P607

P607 $\frac{\mu mole}{Liter}$	P607 $\frac{\mu mole}{g.}$	P607 O $\frac{\mu mole}{liter}$	P607 O $\frac{\mu mole}{g.}$	P607 OR $\frac{\mu mole}{liter}$	P607 OR $\frac{\mu mole}{g.}$
89.5	105	84.8	50.6	85.0	150
73.0	70	69.5	35.0	69.5	105
54.8	52	55.0	26.6	51.5	85
45.3	47	43.5	21.6	43.0	70
38.5	15	34.8	17.3	34.8	52
27.5	25	26.5	11.6	25.6	44
18.6	14	16.6	11.3	16.7	33
9.7	3	8.2	6.0	7.5	25

Note: LC325, S51, S51 O, S51 OR, P607 & P607 OR - 0.050 g.
in 500 ml. solution; LC325 O,& LC325 OR - 0.100 g.
in 500 ml. solution; P607 - 0.150 g. in 500 ml.
solution. Conditions: 30°C, 3 days equil. time.

ADSORPTION OF PHENOL (HIGH CONCENTRATION)

SAMPLES	$\frac{mmole}{liter}$	$\frac{mmole}{g.}$	$\frac{\mu mole}{m^2}$
	354	4.60	4.27
	258	4.20	3.90
LC325	158.5	4.15	3.86
	64.5	3.55	3.30
	364.5	3.55	4.12
	267.0	3.30	3.37
LC325 O	171.0	2.90	3.83
	85.0	1.50	4.12
	376	2.40	2.86
	280	2.00	2.38
LC325 OR	178	2.20	2.62
	77	2.30	2.74
	343	2.85	4.41
	248	2.60	3.87
P607	157	2.15	3.33
	64.5	1.78	2.76
	354	2.30	3.75
	257	2.15	3.51
P607 O	165	1.75	2.85
	72	1.40	2.28
	355	2.25	3.52
	257	2.15	3.36
P607 OR	163	1.85	2.89
	69	1.65	2.58

EFFECTS OF Ca^{++} ON THE ADSORPTION OF BENZENESULFONATE

LC325 with 0.2mmole CaCl$_2$/100ml. soln.		S51 OR with 0.2mmole CaCl$_2$/100ml. Soln.	
$\dfrac{\mu mole}{Liter}$	$\dfrac{\mu mole}{g.}$	$\dfrac{\mu mole}{liter}$	$\dfrac{\mu mole}{g.}$
73.5	265	92.2	78
54.6	254	74.0	60
37.1	229	52.0	80
28.5	215	42.3	77
18.5	215	33.8	62
10.0	200	25.0	50
2.7	173	14.2	58
--	100	5.5	45

P607 with 0.2mmole CaCl$_2$/100ml. soln.		LC325 with 0.4 mmole CaCl$_2$/100ml. soln.	
$\dfrac{\mu mole}{liter}$	$\dfrac{\mu mole}{g.}$	$\dfrac{\mu mole}{liter}$	$\dfrac{\mu mole}{g.}$
79.8	67.3	58.5	365
64.5	51.6	42.0	360
47.5	41.6	25.8	342
40.0	33.3	17.2	328
32.3	26.3	7.6	324
22.8	24.0	0.5	295
14.1	19.6		
6.9	10.3		

EFFECT OF CALCIUM IONS ON THE ADSORPTION OF PHENOL

LC325 with 0.2mmole CaCl$_2$/100ml. soln.	
$\dfrac{\mu mole}{liter}$	$\dfrac{\mu mole}{g.}$
274	1,260
180	1,200
108	920
70	800
31	690
21	540
8	420
2	230

BIBLIOGRAPHY

1. Morris, J.C., Weber, Jr, W.J., "Adsorption of Bio-
   chemically Resistant Materials from Solution. 1."
   P. H. S. Publ. No. 999-WP-11, Environ. Hlth. Series
   AWTR-9, Cincinnatti, Ohio, 1964, 82pp.

2. Weber, Jr, W.J., Morris, J.C., "Kinetics of Adsorp-
   tion on Carbon from Solution," J. Sanit. Eng. Div.,
   Am. Soc. Civil Engrs. 89, (SA2), 31 (1964).

3. Weber, Jr, W.J., Morris, J.C., "Equilibria and Capa-
   cities for Adsorption on Carbon," J. Sanit. Eng. Div.
   Am. Soc. Civil Engrs. 90, (SA3), 79 (1964).

4. Weber, Jr, W.J., Morris, J.C., "Adsorption in Hetero-
   geneous Aqueous System," J.A.W.W.A. 56, 447, April
   (1964).

5. Renn, C.E., Barada, M.F., "Removal of ABS from Heavily
   Polluted Waters," J. A.W.W.A., 129, Feb. (1964).

6. Hansen, R.S., Fu, Y., Bartell, F.E., "Multimolecular
   Adsorption from Binary Liquid Solution," J. Phys.
   Chem., 53, 769 (1949).

7. Kipling, J.J., Wright, E.H.M., "Adsorption on Carbon
   Black from Solutions of Monocarboxylic Acids: the
   Higher Members," J. Chem. Soc, 3382 (1963).

8. Kipling, J.J., Wright, E.H.M., "Adsorption from Binary
   Systems of Limited Concentration Range: Application
   of Some Fundamental Concept," J. Chem. Soc., 855
   (1962).

9. Kipling, J.J., Gasser, C.G., "Adsorption from Liquid
   Mixture at Solid Surfaces," J. Phys. Chem., 64, 710
   (1960).

10. Parfitt, G.D., Willis, E.J., "Adsorption at the Solid-
    Liquid Interface I. Alkylbenzenes on Graphon from
    Solution in n-Heptane," J. Phys. Chem., 68 (7), 1780
    (1964).

11. Graham, D., "Characterization of Physical Adsorption Systems III. The Separate Effect of Pore Size and Surface Acidity Upon the Adsorbent Capacities of Activated Carbon," *J. Phys. Chem.*, 59, 896 (1955).

12. Zarifyanz, Y.A., Kiselev, V.F., Lezhnev, N.N., Nikitina, O.V., "Interaction of Graphite Fresh Surface with Different Gases and Vapours," *Carbon*, 5, 127 (1967).

13. Boehm, H.P., Diehl, E., Heck, W., Sappok, R., "Surface Oxides of Carbon," *Angew. Chem. Intern. Ed. Engl.* 3 (10), 669 (1964).

14. Boehm, H.P., "Functional Groups on the Surfaces of Solids" *Angew. Chem. Intern. Ed. Engl.*, 5 (6), 533 (1966).

15. Puri, B.R., "Chemisorbed Oxygen Evolved as Carbon Dioxide and its Influence on Surface Reactivity of Carbon," *Carbon*, 4, 391 (1966).

16. Studebaker, M.L., Huffman, K.W.D., Wolfe, A.C., Nabors, L.G., "Oxygen-Containing Groups on the Surface of Carbon Black," *Ind. Eng. Chem.*, 48, 162 (1956).

17. Villars, D.S., "Studies on Carbon Black II. Grignard Analysis," *J. Am. Chem. Soc.*, 70, 3655 (1948)

18. Hallum, J.V., Drushel, H.V., "The Organic Nature of Carbon Black Surfaces," *J. Phys. Chem.*, 62, 110 (1958).

19. Rivin, D., "Use of Lithium Aluminum Hydride in the Study of Surface Chemistry of Carbon Blacks," 4th Rubber Tech. Conf., London, 1962, 12pp.

20. Garten, V.A., Weiss, D.E., Willis, J.B., "A New Interpretation of the Acidic and Basic Structure of Carbon," *Australian J. Chem.*, 10, 295 (1957).

21. Kipling, J.J., Wright, E.H.M., "Physical and Chemical Adsorption of Formic And Acetic Acid by Spheron 6," *J. Phys. Chem.*, 67 (9), 1789 (1963).

22. Giles, C.H., MacEwan, T.H., Nakhwa, S.N., Smith, D., "Studies in Adsorption Part XI. A System of Classi-fication of Solution Adsorption Isotherms and its Use in Diagnosis of Adsorption Mechanism & in Mea-surement of Specific Surface Areas of Solids," J. Chem. Soc., 3973 (1960).

23. Ottewill, R.H., Tiffany, J.M., "The Adsorption of Long Chain Acids on the Rutile from n-Heptane," J. Oil and Colour Chemists' Assn., 50 (9), 844 (1967).

24. Zettlemoyer, A.C., Skewis, J.D., Chessick, J.J., "The Adsorption of Calcium Ions to Surfactant Films on Graphon," J. Am. Oil Chem. Soc., 39, 280 (1962).

25. Coughlin, R.W., Ezra, F.S., "Role of Surface Acidic Groups in the Adsorption of Organic Pollutants on the Surface of Carbon," Environ. Sc. & Tech., 2 (4), 291 (1968).

26. Weber, Jr, W.J., Morris, J.C., Stumm, W., "Determina-tion of ABS by Ultraviolet Spectrophotometry," Anal. Chem., 34 (13), 1844, Dec (1962).

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