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ADSORPTION OF LARGE COMPOUNDS ON ACTIVATED CARBON

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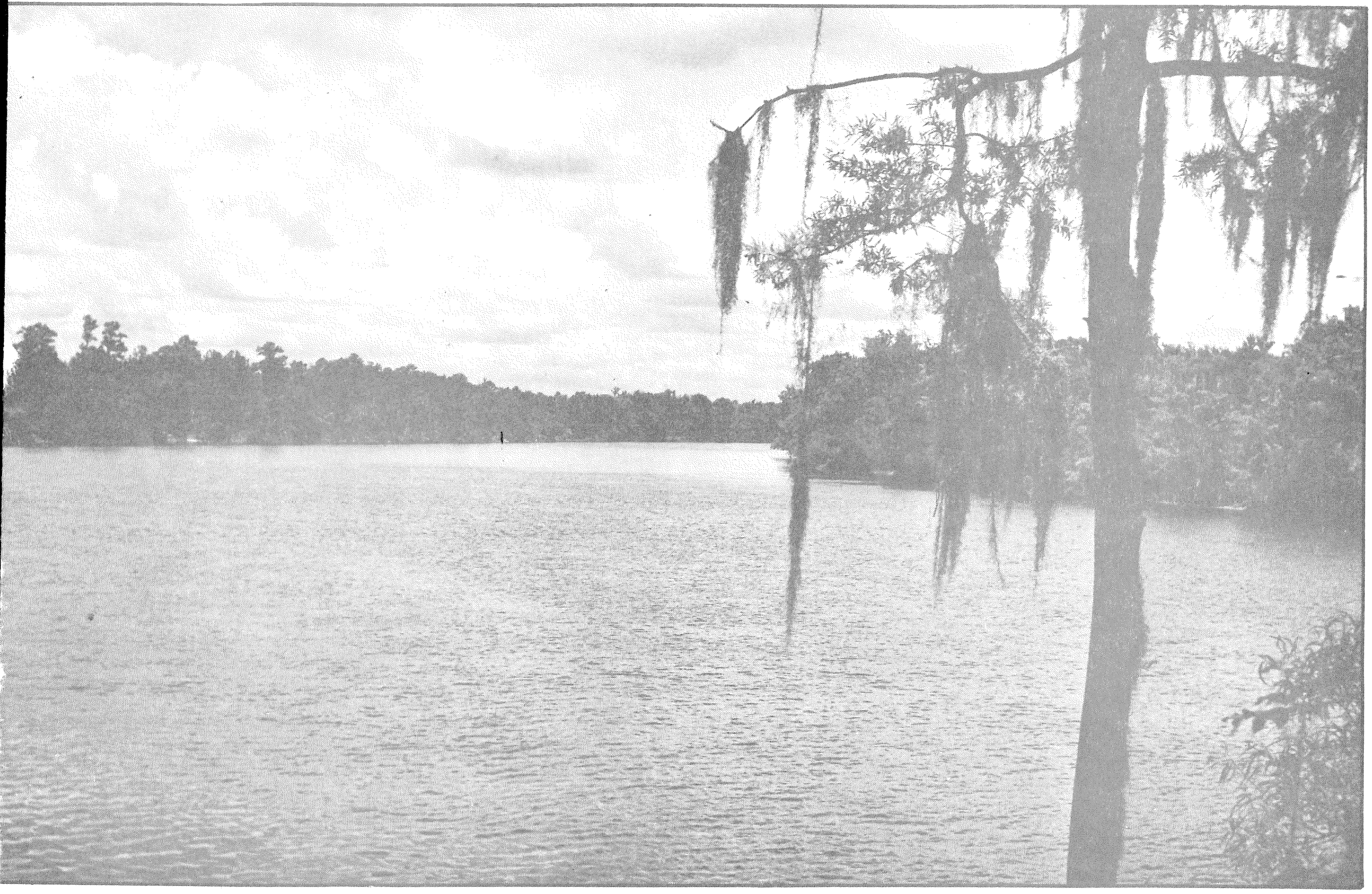

UNIVERSITY OF FLORIDA

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ABSTRACT

As Florida's water demand increases due to population growth and to increased per capita consumption, less desirable sources of water will be used, requiring additional treatment for the removal of organic compounds. In addition, wastewaters will require additional treatment to remove organic compounds. In both cases, activated carbon adsorption is the process most likely to be applied. Most of the organics present in natural waters and biologically treated wastewaters are large compounds (i.e. molecular weight [MW] > 500), and little is known about large compound adsorption.

An optimum size of adsorbate molecule appears to exist, since the 5200 MW inulin adsorbs better than the 342 MW sucrose and the 20,000 MW xylan on all three adsorbents evaluated, including the small-pored petroleum pitch carbon. When adsorbing the xylan, even the large-pored lignite carbon's capacity was much reduced. No chromatographic effect was noted in continuous column studies at 1 and 2 gpm/ft2. Premature exhaustion may exist as proposed in previous studies, but additional studies are needed at longer contact times (> 30 minutes); in general, carbon use decreases with increased contact time. More studies are needed.

INTRODUCTION

Water and wastewater problems are likely to become very important issues in Florida in the near future; due to its rapidly expanding population. The problem is intensified since most of the population growth is occurring in the southern coastal regions of the state where the least potable water is available. Groundwater is used extensively for water supply, but additional water withdrawals may threaten existing supplies by permitting salt water to intrude into the fresh water aquifers, rendering them useless. Due to the large number of hazardous waste disposal sites within the state, the potential for contaminating the groundwater is great. And some water supply wells have been abandoned due to pollution from the surface. Groundwater supplies are limited, and diligence is needed to protect the existing systems.

Many communities use surface waters to supply their water; surface water sources could be used more extensively in Florida, but water quality problems are likely to result, as well as legal problems associated with transferring water from one drainage basin to another, since most of the surface water is in the northern part of the state. Many surface waters are highly colored due to decaying vegetation, the color is not only aesthetically objectionable, but produces trihalomethanes, which are believed to be carcinogenic compounds. Special treatment will be required to remove this color, with both activated carbon adsorption and chemical coagulation the most likely processes. In addition, surface water use will require protection from wastewater discharges, especially as the population expands.

More extensive wastewater treatment will be required when the waste is discharged into a stream used for potable water supply or when the waste is used to recharge the groundwater, whether to protect it from salt water intrusion or as an ultimate disposal method. Undoubtedly, concern for trace organic compounds in these wastes will require activated carbon adsorption as a treatment step.

Activated carbon adsorption is a very effective process for removing organic compounds from water. In potable water treatment, activated carbon has been used for years to remove taste and odor causing compounds and for removing color bodies (1). When used in these applications, powdered activated carbon is usually added in the normal water treatment processing steps; if the water has extremely high levels of contaminants, then granular activated carbon has been used to replace the sand in the rapid sand filters (2) -- providing better, more economical treatment. Recently adsorption has been extensively evaluated for the removal of trihalomethane precursors and synthetic organic chemicals from our potable waters (3,4,5), with the U. S. Environmental Protection Agency proposing it as a treatment requirement for all water plants providing water to communities greater than 75,000 people (6). For these applications, an additional processing step would probably be added to the treatment system, rather than replacing the sand with activated carbon as is done for high levels of taste and odor producing compounds and for high color levels, adding substantially to the capital and operating costs of the water treatment system (7).

When a groundwater becomes contaminated by synthetic chemicals and the water source is not abandoned, the water can be processed to acceptable quality using granular activated carbon systems (8). Portable systems can be taken to the site and installed in a short time, providing excellant removal of many compounds (9).

In wastewater treatment, activated carbon adsorption is used to remove refractory organic compounds when a high quality water is needed such as for South Lake Tahoe (10) or Water Factory 21 (11). It is also used with chemical addition to replace "normal" secondary treatment plants with physical/chemical treatment processes (12), where the adsorption system is used to remove the organic compounds. Industry can also use activated carbon to remove toxic and nondegradable compounds before discharging them into sewers (13), so they won't destroy or inhibit the biological treatment system -- industrial applications are likely to increase dramatically if the U.S.E.P.A. sets strick limits on toxic compound discharges.

In many potable water supplies, a variety of organic compounds exist in the water, with over 250 chemicals identified in the nation's potable water supplies (14). Extensive efforts are underway to identify the components of a water, but only a small fraction of the total organic carbon of a water is identifiable (15). These compounds are generally small molecules (smaller than 200 atomic mass units). The remaining compounds are frequently classified as humic substances which include both humic and fulvic acids (humic acids are less soluble under acidic conditions). Their molecular weight distribution has been evaluated using gel chromatography (16, 17, 18). Most of the compounds have a molecular weight greater than 500, with many being considerably larger than 10,000.

In wastewaters, only a small fraction of the organic carbon present is identifiable as specific compounds -- most of the remaining compounds are large compounds. Attempts have been made to identify the families of compounds, with proteins, carbohydrates, lignins, and tannins sometimes identified along with the molecular weight distributions.

The purpose of this study is to provide basic background adsorption equilbria data for some specific high molecular weight model compounds; this should indicate which families of compounds could potentially be a problem for adsorption processes. In addition, how well the model compounds adsorb on different activated carbons will be evaluated to determine if a particular carbon appears better suited for large compound adsorption. Fixed-bed adsorption studies will also be performed with a mixture of compounds to determine if the compounds fractionate by molecular weight within the adsorber. [This could be due to the slower diffusion of the larger compounds, causing the large compounds to penetrate deeper into the bed where they adsorb and block the adsorbent's pores; thereby preventing additional adsorption when the smaller compounds reach that point in the column. This phenomenon is referred to as premature exhaustion and results in larger than expected carbon usage (19)].

BACKGROUND

There is not much information available on the adsorption of large molecular weight compounds, most of the available information is for humic substances or fractionated wastewater. In addition, some information is contradictory.

Humic Substances: These materials are very complex, source-dependent organic substances. They are classified as humic or fulvic acids, with the humic acids being less soluble compounds which are separated from the fulvics by lowering the pH to 2, where the precipitate that forms is humic acid.

The large fraction (MW > 4000) of lake water was found to adsorb better on aluminum oxide solids than the small fractions (MW < 400); their adsorption is more pH dependent (20). Adsorbing fulvic acids extracted from Michigan peat onto activated carbon finds the large materials (MW > 50,000) adsorbed less than the smaller ones (MW < 1000). There are indications that the small fractions associate with the large ones in solution when adsorbing, since the unfractionated sample's adsorption pattern was similar to that of the large fraction's (21). The adsorption of the small compounds correlates with the pore volume in pores smaller than 7 nanometers for the nine activated carbons tested, and the large compounds's adsorptive capacity correlates with the pore volume in pores smaller than 40 nanometers. Carbons with most of their pore volumes in the larger diameter pores would be more suitable for adsorbing large compounds. Both adsorption capacity and adsorption rate increased with decreasing molecular weight for the fulvics studied. Other researchers have also found adsorptive capacity to increase with decreasing molecular weight (22, 23). Unfractionated soil fulvic acid adsorbed similar to the smallest molecular weight fraction (MW < 5000), while the soil humic acid's adsorption was similar to the middle molecular weight fraction's (5,000 - 50,000) (23). Removals depend upon the source of humic materials (24).

The solution's chemical conditions significantly affect the results. Humic acid was 10 times more adsorbable from tap water than from deionized-distilled water, indicating that co- and/or counterions are important factors (25). Magnesium ions enhanced adsorption capacity more than calcium; hypochlorite ions also increased capacity. Others have found little adsorption of humics in the absence of salts, with the anions having no effects (26). The cations were most important, with Ca enhancing adsorption more than Mg which had a greater effect than Na. Cation effects were much reduced at low pH values. In another system phosphate was found to greatly increase adsorption capacity (2 to 3 times) (23). The humic substances remaining after precipitation of humic materials with alum, adsorb substantially better than those present before treatment (27, 21). Solution pH is also important, with studies finding adsorption capacity to increase with decreasing pH from 11 to 2 (23) while others found an optimum pH when using an aluminum oxide adsorbent instead of activated carbon (20). Humics were found to have an optimum adsorption pH in a study testing only 3 pHs, since the lowest pH (4.5) resulted in a lower adsorptive capacity than the two higher pHs (28).

Humic substances have a significant adverse effect on the adsorption of chlorophenols (29), while only exhibiting a slight effect on the adsorption of phenol at neutral pH (30). A larger adverse effect on phenol adsorption resulted at pH 9, but this is probably due to the ionization of the phenol as its pKa is approached (31). At pH 2 ,no interference with adsorption was observed (30), the humic materials would be expected to adsorb to a greater extent at pH 2 since they become insoluble; but the humic materials were believed to become insoluble colloids and therefore did not adsorb in the normal sense, but behaved in a manner similar to other colloids (30). Other colloids (clay or polyelectrolytes) added to the phenol system did not interfere with phenol adsorption by adsorbing and blocking the pores (30).

Few adsorption column studies were reported. In one study a short empty-bed contact time was used (1.6 minutes, approximately equal to a 5 inch deep adsorber with a flow of 2 gpm/ft2) and a "rapid" humic acid breakthrough was observed with only a small amount of material adsorbed (0.23 mg/g) (28). Humic substance adsorption has been modeled, with only 40 percent of the carbon's equilibrium capacity utilized at 80% breakthrough due to slow adsorption (32). Model studies found the system insensitive to the film transfer coefficient and, in the early stages of the breakthrough curve, to the surface diffusion coefficient; during the later stages of breakthrough, the system becomes sensitive to surface diffusion. Pretreatment of the humic substances with alum increases the service time of the adsorber by 14 to 22 times (32)! Because of the slow surface diffusion, long empty-bed contact times are required to contain the mass transfer zone.

Wastewater Materials: Several studies exist using wastewater compounds. In an early study, compounds larger than 1200 MW were claimed not to adsorb, with only the compounds about 400

MW and smaller adsorbed (33). They hydrolyzed the larger compounds to smaller ones using lime and a sufficient reaction time; then the hydrolyzed organics were adsorbed with far better treatment resulting. Similar results were obtained in another physical-chemical scheme evaluated at the pilot level (34). In addition, a study on virus removal found the organic removal to increase substantially after lime treatment, like in the hydrolysis treatment (35). Many others have found the smaller compounds to account for most of the non-adsorbing material (36, 37,38, 39). These studies were more detailed research studies; they all used secondary effluents. The studies showing the small materials to be more adsorbable used physical/chemical pilot plant influents and effluents, except for the virus study which used a secondary effluent.

In column studies, all MW fractions were found to be adsorbable to some extent, with 52 percent of the smallest compounds and 35 percent of the larger compounds adsorbed; the intermediate size was 90 percent removed (38). The large compounds (MW > 50,000) that were not adsorbed were carbohydrate-like materials. Column studies performed on size-fractionated biologically-treated wastewaters found the smallest compounds not to adsorb; but, if the material was fractionated after adsorption, all fractions adsorbed to some extent in the columns (37). Mean cell residence time greatly affects the quantity of the largest compounds, with decreasing mean cell residence times resulting in more large compounds, and therefore poorer overall removals by adsorption.

Batch kinetic and equilibria studies were performed on three fractions of an extensively treated industrial wastewater (60 hours hydraulic residence time, sludge age greater than 10 days) (19). This waste was used in a previous pilot study where adding a second column in series with the first adsorber resulted in a 70 % increase in carbon usage, rather than the expected reduction in use (40); it was referred to as premature exhaustion. Pilot scale ultrafiltration and reverse osmosis was used to fractionate the waste prior to the adsorption studies. A majority of the material (48%) passed through the ultrafiltration membrane, but was rejected by the reverse osmosis membrane (about 342 to 6500 MW). This fraction adsorbed best (79%), while the smallest material adsorbed least (55%); the large fraction was 62% adsorbable (19). Adsorption energy increased with increasing molecular weight, indicating that the larger compounds are more strongly adsorbed and therefore are more difficult to displace. The larger compounds adsorb at a slower rate, as would be expected. This study proposed that the large compounds penetrate far deeper into the adsorber than the smaller compounds before adsorbing. Deep in the adsorber, there is less competition for adsorption sites and they slowly adsorb,but over a period of time they have utilized a large portion of the adsorbent's capacity. Due to their size, they effectively block the pores of the carbon and since they are stongly adsorbed, they cannot be displaced.

Gums were tested in dye wastes for their effects on adsorption, with the large gums (MW > 200,000) having a positive effect on the activated carbon system at 65 to 100 mg/L levels, but having an adverse effect at lower concentrations -- no reasons were given (41). The effect of pH on the adsorption of lignosulphate and tannins were evaluated in real industrial wastes (42), with lignin and tannins both removed better from their respective wastes at higher pHs.

Pure Compounds: Lysozyme (MW about 13,900) and bovine serum albumin (MW about 67,500) occupy nearly the same surface area on activated carbon when adsorbed from solution, even though one is 4 times larger (43). These proteins were irreversibly adsorbed. Effective adsorption diffusivities were about 6 percent of the bulk diffusivity for the lysozyme and 0.7 percent, for the bovine serum albumin. Maximum adsorption occurred at their isoelectric points.

The equilibria and kinetics of adsorbing a series of polyethylene glycols (PEGs, MW 194 to 2,490,000) were studied using coconut-based and lignite-based activated carbons (44). The coconut carbon has most of its pore volume in micropores (in this case >70% of the volume is in pores smaller than 3 nanometers), this does not permit the larger compounds to adsorb as well, with adsorption capacity decreasing for PEGs larger than 1500 MW. With the lignite carbon (>70% of its pore volume is in pores larger than 3 nanometers), adsorption capacity increased with increasing MW up to 1500 MW, where the maximum loading was achieved. Increasing MW above this value did not change the adsorption capacity, so the same surface area or pore volume is accessible for all these large compounds. The effective diffusion coefficient decreased with increasing MW, with the coconut carbon's diffusivities larger than the lignite carbon's. Using these values in calculations for a "typical" water treatment application found that compounds much smaller than 10,000 MW would pass through the adsorber without having a chance to adsorb, longer contact times are needed.

Three different molecular weights of polyvinyl acetate were adsorbed on activated carbon; the smaller compounds took longer to reach "complete" equilibrium; the 170,000 MW molecule took 20 minutes, while the 22,000 MW material took 60 minutes (44). Adsorption equilibria capacities also increased with decreasing molecular size; the 170,000 MW material had an ultimate capacity of 0.06 g/g, the 68,000 MW material's capacity being 0.11 g/g , and the 22,000 MW material's capacity being 0.19 g/g.

Adsorption equilibria were evaluated for different MW fractions of dextran (a carbohydrate), with adsorption capacity at a maximum for MW of 6000, higher MW fractions (up to 500,000) resulted in lower loadings (45). Loadings of 400 mg/g were obtained at equilibria concentrations of 10,000 mg/L.

To summarize, many small compounds (MW < 500) and very large compounds (MW > 20,000) are not very adsorbable, whether they are humic materials or fractionated wastewater components. The most adsorbable fraction is the 1000 to 10,000 MW materials, with up to 90% of it adsorbable. For many activated carbons, this size material corresponds to the size material that adsorbs to a maximum capacity when adsorbing a homologous series of compounds. The adsorption rate in batch studies decreases with increasing MW, with little or no removal expected in a "typical˜ filter-adsorber used for water treatment (short contact time); although in column studies all fractions are removed to some degree, even if they were not removed in batch studies. Solution chemistry is very important for compound adsorption, with calcium and magnesium cations apparently the most important species.

EXPERIMENTAL

Materials: The following chemicals were obtained from either Sigma Chemical, Aldrich Chemical, or Fisher Scientific for use as received:

polysaccharides:	sucrose	(342 MW)
	inulin	(5200 MW)
	xylan	(20,000 MW)
protein:	egg albumin	(45,000 MW)
synthetics:	phenol	(94 MW)
	polyethylene glycol	(400 MW)
	polyacrylic acid	(5,000 MW)
	polyvinyl pyrrolidone	(10,000 MW)

The following activated carbons were used as provided by the manufacturers:

Filtrasorb 400 - Calgon Corporation

Hydrodarco 4000 - ICI America

BAC-SQ - Kureha Chemical Co. (Japan)

Filtrasorb 400 (F400) is a bituminous coal-based activated carbon with an approximate surface area of 1100 m2/g; Hydrodarco 4000 (HD4000) is a lignite-based carbon with a surface area of 700 m2/g; and BAC-SQ is a petroleum pitch-based carbon with a surface area of 1100 m2/g. The petroleum carbon has the smallest pores, with 67 percent of its pore volume in pores smaller than 2 nanometers (Table I). F400 has 47 percent of its pore volume in pores smaller than 2 nanometers, and HD4000 has only 2 percent of its volume in these small pores, with 60 percent of its volume in pores larger than 10 nanometers. If pore volume is the main factor for the adsorptive capacity of the molecules and surface chemistry is a minor consideration, the largest molecules should be able to penetrate and adsorb better in the HD4000, then F400, which would be better than BAC-SQ; conversely, the smallest molecules should adsorb better in the BAC-SQ, followed by the F400, followed by HD4000. All activated carbon for the equilibria studies was pulverized in a Waring blender, sieved through a U.S. Standard Sieve No. 120 (<125 microns), washed with distilled water until the supernatant was clear, dried at 105 C for 24 hours, and stored in sealed bottles until used.

TABLE I

Pore Volume Distribution for Adsorbents

Pore Size nanometers	Percent of Total Pore Volume		
	BAC-SQ	F400	HD4000
< 2	67	47	2
2 - 3	11	22	12
3 - 5	7	10	11
5 - 10	6	8	15
> 10	9	13	60

MilliQ deionized water was used to prepare all solutions; for the equilibrium studies using low initial solute concentrations (10 - 20 mg/L), the deionized water was filtered through an 18-inch deep granular activated carbon bed prior to use, to remove any organic compounds that may be present. No buffer was used since some studies indicate their effects were small (46).

Equilibria Studies: Initial equilibria studies were performed using an oscillating platform shaker operating at 150 rpm. Although the equilibrium time tests were based on this system, the mixing pattern of the activated carbon in solution did not appear satisfactory, as the activated carbon partially settled in the center of the flask. Wooden racks were constructed and mounted on a metal frame on the oscillating shaker table, the racks held 120 ml Wheaton bottles at a 45° angle - this was done to induce turbulence (Figure 1); also, a drum was modified to hold wooden racks of Wheaton bottles, with the drum then placed on a dual roller device to rotate at low rpms (about 15 rpm was the slowest speed that our system could maintain - Figure 2). Both systems provided better mixing patterns, with no difference noted among the isotherms performed on all three systems.

Albumin was used in an initial test to determine the time required for the largest compound (45,000 MW) to reach equilibrium. During the first two hours of shaking, the albumin concentration decreased from 60 mg/L to nearly 30 mg/L, and after 5 days it had dropped to 12.5 mg/L. In the next 9 days, the concentration decreased to 11 mg/L, so it appeared 14 days would be sufficient; but to ensure sufficient equilibration, 21 days of mixing were provided. This time is more than adequate based on a comparison to the times used by others (one to seven days) who studied large compound adsorption (23, 25, 28, 30, 36, 38).

At the completion of 21 days of mixing, the carbon was settled and then a sufficient quantity of solution was filtered through a Whatman GF/C filter pad; the albumin solution did not filter well and required centrifuging rather than filtration to remove the carbon fines from solution.

Column Studies: Fixed-bed adsorber studies were performed in 25mm internal diameter glass columns of varying

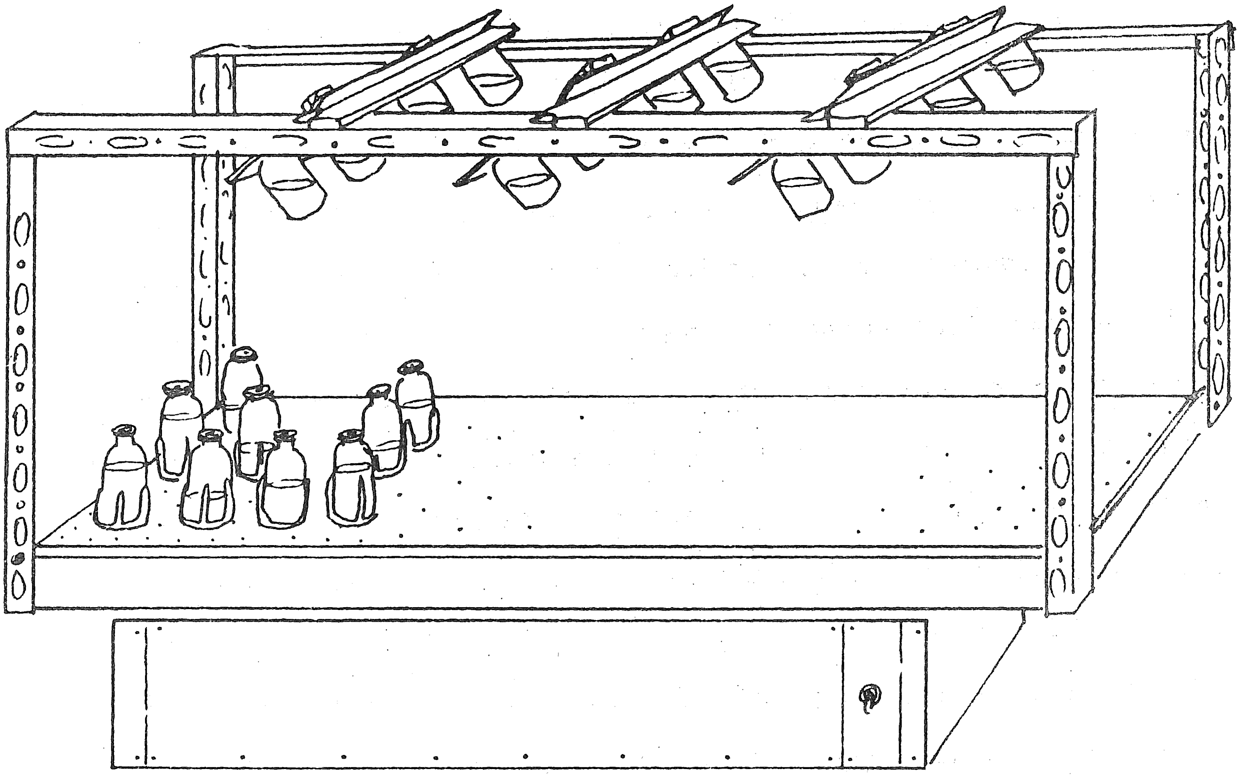

FIGURE 1: MODIFIED SHAKER TABLE FOR ISOTHERMS

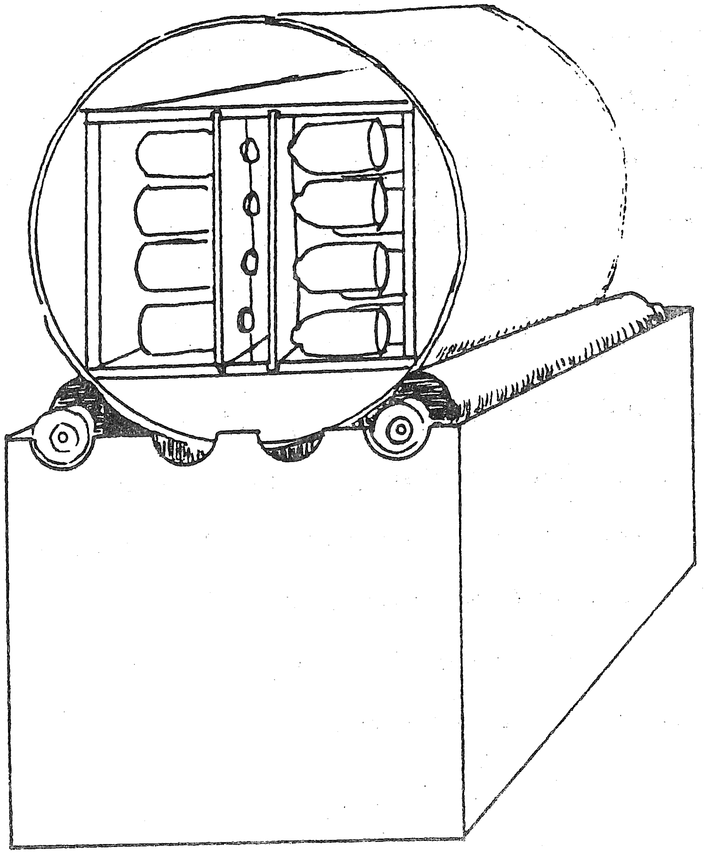

FIGURE 2: ROLLER APPARATUS FOR ISOTHERMS

lengths to provide the desired contact times. Filtrasorb 400 was used and has an average particle diameter of 1 mm, resulting in a 25:1 column to particle diameter ratio -- this is considered by many to be sufficient to eliminate wall effects (47). Masterflex tubing pumps were used to control the flow to the adsorbers, with desired flows of 0.5, 1.0, 2.0, and 4.0 gpm/ft2. Samples were taken after each column and analyzed for the specific components as indicated below.

Analytical Methods: All single component equilibrium samples were analyzed using an Oceanographics International Total Organic Carbon Analyzer Model 525 B. Both the direct inject and the ampule techniques were used; when the final equilibrium solution concentration was greater than 5 mg/L, the direct inject technique was used, when smaller values resulted, the ampule technique was used. Standard curves were run each time analyses were performed, with the standard prepared using the compound being studied; so results are reported as mg/L as compound and not TOC. When mixtures were used, each mixture contained a polysaccharide (inulin or xylan) which could be determined directly using the phenol-sulfuric acid test (50). Phenol was a second component and ultraviolet spectroscopy (Perkin-Elmer dual beam spectrophotometer Model 5200) was used to determine its concentration. The third component in the mixture was calculated by measuring the solution's TOC and subtracting the TOC response of the equivalent concentrations of the polysaccharide and phenol and then converting the remaining TOC response into the third compound's concentration.

RESULTS AND DISCUSSION

Equilibria Tests:

Equilibrium isotherms were performed on the three carbohydrates using all three activated carbons: F400, HD4000, BAC-SQ. Since F400 is the most frequently studied adsorbent, it was used to adsorb additional large compounds for comparative purposes. The Freundlich adsorption equilibrium model was used to represent the data, since it has been found to fit many data successfully. Unfortunately it is an empirical model; but, a theory has been proposed that results in the Freundlich isotherm equation (49). The theory is based on adsorbing substances on a surface with heterogeneous surface energies, therefore the heat of adsorption varies with surface coverage. The Freundlich equation is:

$$X = K C^{1/n}$$

Where, X is the loading of the solute on the adsorbent in mg/g; C is the equilibrium solution concentration of solute in mg/L; and K and n are empirical constants. K is proportional to the adsorption energy, with the larger the value, the greater the adsorption energy; and n is related to the intensity of adsorption, with the greater the n, the more intensely the material is adsorbed (49). The Freundlich isotherm is used to represent the adsorption of the large compounds on the various carbons, although its ability to fit the data was not always good. The Freundlich constants are provided in Table II.

TABLE II

FREUNDLICH CONSTANTS

Compound	MW	Adsorbent	# of data	Freundlich Constants	
				K, mg/g	n
Sucrose	342	F400	11	.95	.64
		HD4000	9	3.03	2.27
		BAC-SQ	10	7.50	1.66
Inulin	5200	F400	4	37.2	4.80
		HD4000	7	69.6	5.63
		BAC-SQ	7	84.7	4.35
Xylan	20,000	F400	13	1.66	2.82
		HD4000	5	2.07	1.38
		BAC-SQ	5	1.5E-06	.29
PEG 400	400	F400	10	40.8	3.89
		HD4000	6	29.1	4.38
		BAC-SQ	5	18.8	1.53
PAA	5000	F400	8	6.1E-05	.34
PVP	10,000	F400	6	.01	.48
Albumin	45,000	F400	6	4.5E-04	.35
Phenol	94 (from reference 46)	F400		78.1	4.72

PEG - polyethylene glycol
PAA - polyacrylic acid
PVP - polyvinyl pyrrolidone

A wide variation in both Freundlich K and n constants exists for the large compounds tested. The adsorption energy term, K, varies by nearly 8 orders of magnitude, with three compounds being essentially non-adsorbable or poorly adsorbed on a particular adsorbent: xylan was non-adsorbable on BAC-SQ; PAA, PVP, and albumin were poorly adsorbed on F400. Inulin and PEG 400 were both adsorbed strongly on all carbons. Adsorption intensity terms varied from .29 to 5.6, with values greater than

1 required for favorable adsorption (49). All three of the additional large compounds adsorbed on F400 were poorly adsorbed, as indicated by the unfavorable n terms. The xylan was also unfavorably adsorbed on BAC-SQ, it probably could not penetrate its narrow pore structure. In addition, sucrose's n value is less than 1 for F400, but this is misleading since a two-sloped isotherm plot resulted, and these values are for the steep portion of the curve; a horizontal curve results at higher concentrations.

Sucrose adsorption follows a pattern expected for the adsorption of small molecules based on previous experience (50) and published data using carbons with similar pore structures, such as a coconut-based (Columbia carbon) or another petroleum carbon (Witco carbons)(51, 52); the small pore diameter petroleum-based carbon has the greatest adsorptive capacity, followed by the bituminous-based, and, with a considerably lower capacity, the lignite-based carbon (Figure 3). Since the petroleum and bituminous coal carbons have similar surface areas, the main difference is in the pore size distributions (or possibly the surface chemistry which was not evaluated in this study) -- the smaller pores apparently exert stronger adsorption forces on the solute, permitting greater adsorption. With the F400 carbon, a two-sloped isotherm results, with the maximum capacity obtained at an equilibrium solution concentration of about 80 mg/L and no additional adsorption occurring with increased concentrations. Multisloped isotherms have been observed by others (53, 54). Sucrose adsorption

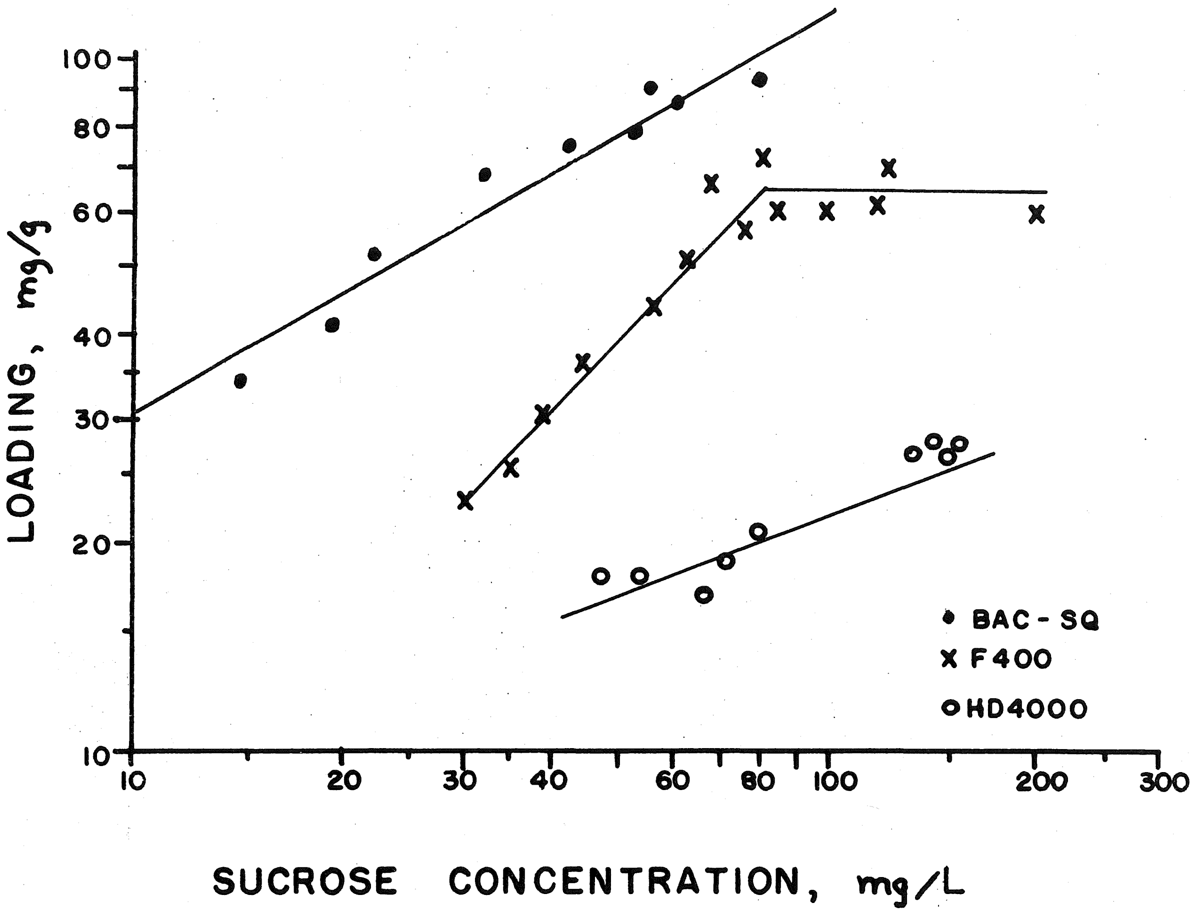

FIGURE 3: SUCROSE ISOTHERM

follows the adsorption pattern expected for smaller compound adsorption.

BAC-SQ's adsorptive capacity is nearly double F400's capacity for inulin (MW 5200), a result that is similar to those obtained for sucrose (Figure 4). The lignite carbon's capacity is is considerably improved relative to the other carbons, since its capacity for the inulin is greater than F400`s and is about two-thirds of BAC-SQ's (it was about 20% of BAC-SQ's capacity for sucrose). Inulin's larger size (5200 MW) was expected to limit its access into most of BAC-SQ`s pores, and to a large amount of F400's; so the lignite carbon was expected to perform best due to its better performance for the adsorption of humic substances of this size (21). Favorable adsorption behavior is exhibited with good adsorption capacities for all three activated carbons. The small pores of BAC-SQ are large enough to permit access of the inulin, since approximately 40% of the total pore volume would be occupied (if inulin's adsorbed specific gravity is 1.5). HD4000's pores are better suited to the adsorption of this polysaccharide; the larger molecule fills the pores more completely, leading to stronger adsorption energies (K constant increased 20 times) and therefore to greater capacities.

Xylan (MW 20,000) does not adsorb on BAC-SQ, while F400 and HD4000 capacities are considerably reduced relative to those with inulin (Figure 5). The large-pore lignite carbon has a much greater capacity than F400. This pattern was expected from the pore size distributions and the results with humic substances (21). With the very large molecules, to obtain better adsorption, a larger pore size distribution is required to obtain

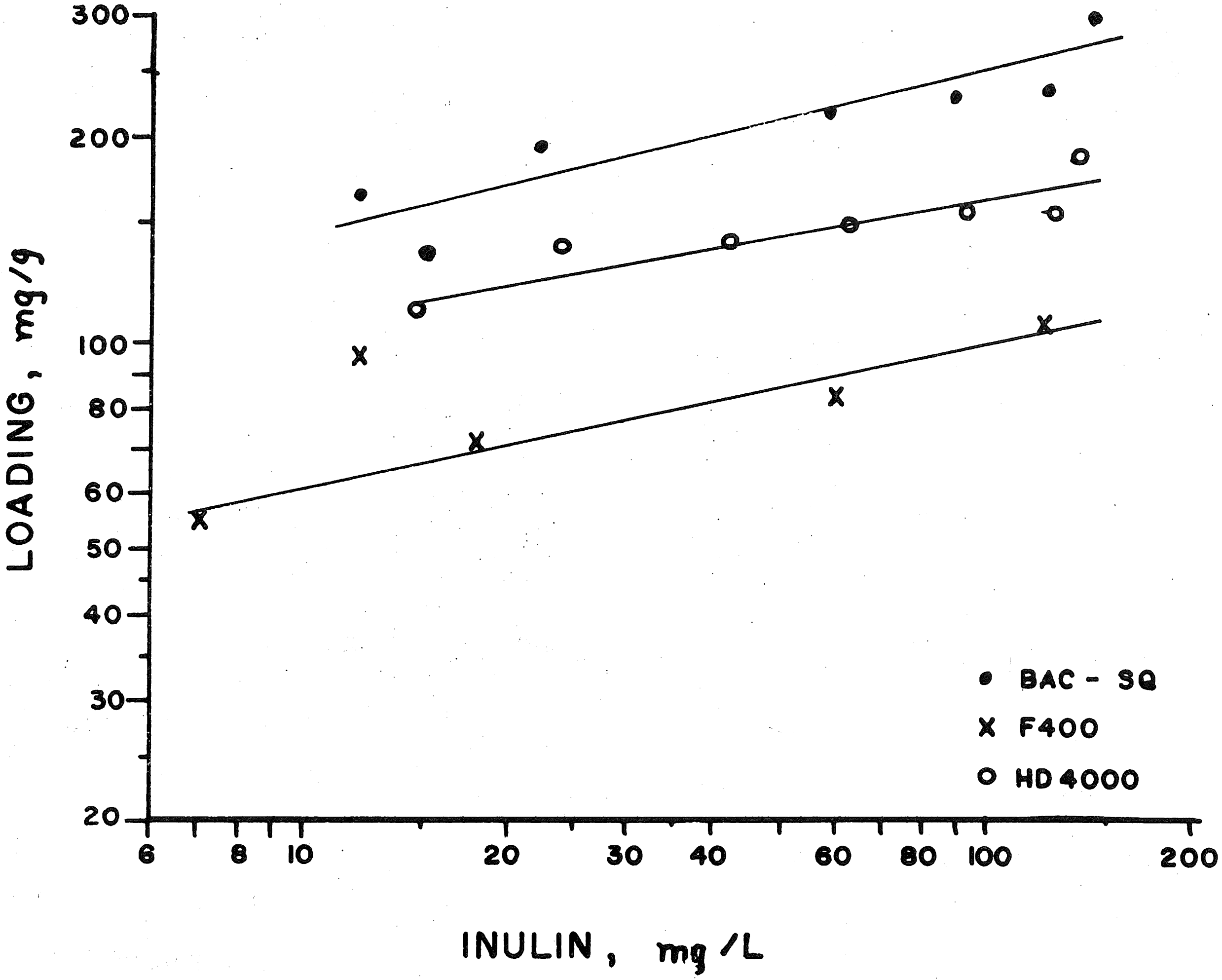

FIGURE 4: INULIN ISOTHERMS

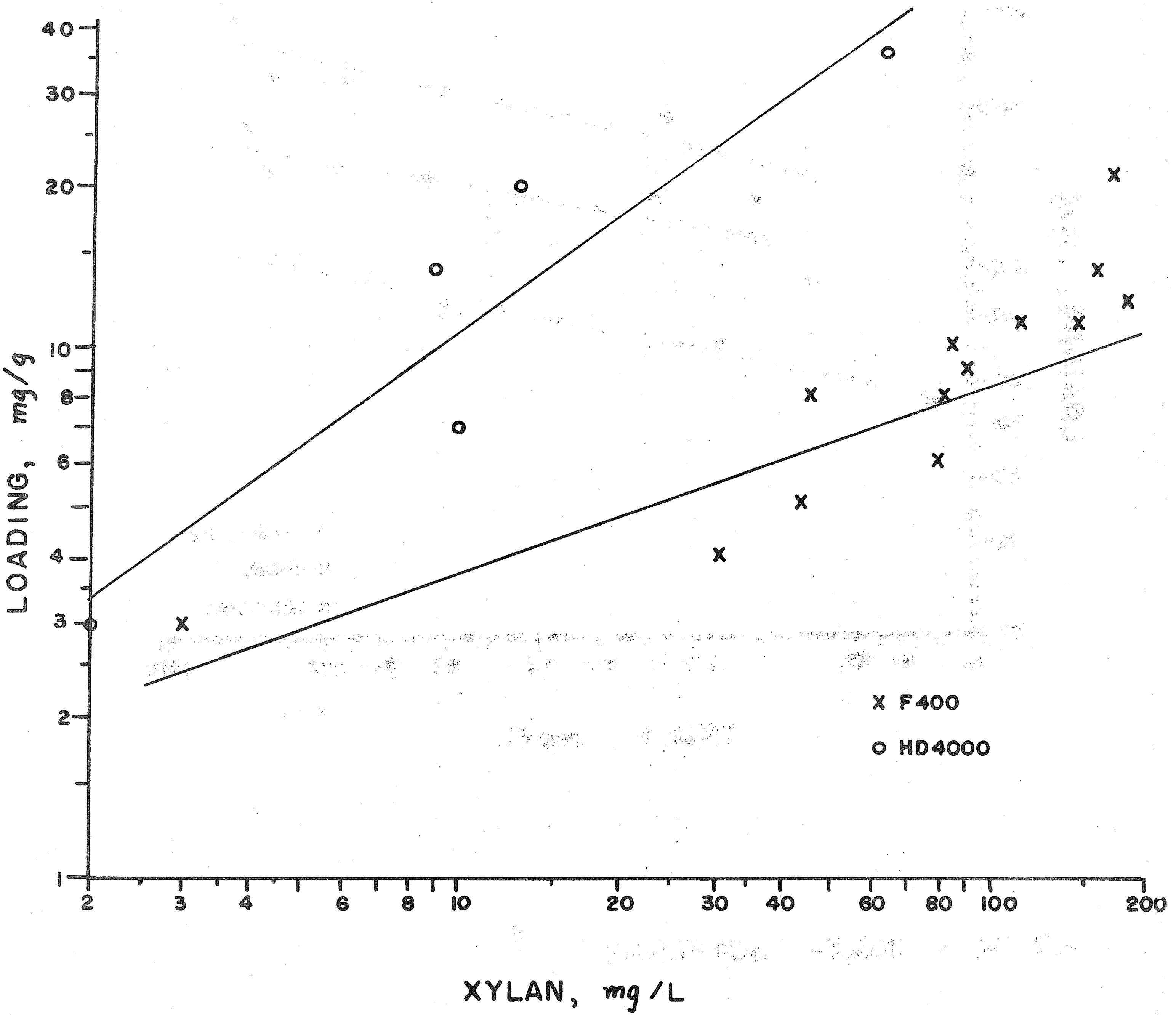

FIGURE 5: XYLAN ISOTHERMS

the best adsorption capacity. But, its capacity is not large and there may be better means of removing these compounds, such as chemical coagulation or precipitation.

The small, narrow pore size distribution of BAC-SQ was expected to provide excellent adsorptive capacity for the sucrose molecule, with progressively poorer adsorption of the other polysaccharides. Sucrose adsorption is favorable on this carbon, with a maximum observed capacity of nearly 100 mg/g; but the 5200 MW inulin's adsorption is surprisingly good with a maximum capacity of 300 mg/g and a nearly horizontal slope in a Freundlich plot (Figure 6), indicating favorable adsorption. The xylan's adsorption (MW 20,000) is basically non-existent, which is not a surprise since it should be excluded from this carbon due to the narrow range of pore sizes. Use of this adsorbent finds the molecules of 5200 MW capable of penetrating to pores smaller than 3 nanometers and adsorbing there, with this adsorption stronger than for the smaller molecules; therefore, this size material should be effectively removed from water and wastewater in studies with all activated carbons. Studies with fractionated materials found this fraction to be adsorbed best (19, 37, 38).

Adsorption of the three polysaccharides on F400 exhibits the same pattern, except the xylan adsorbs to an appreciable extent (Figure 7). Inulin adsorbs best, with a maximum observed capacity of 105 mg/g and a very shallow slope. Sucrose adsorption follows the Freundlich pattern up to about 80 mg/L equilibrium solution concentration, where its capacity plateaus at 60 - 70 mg/g. The xylan's adsorption pattern is favorable,

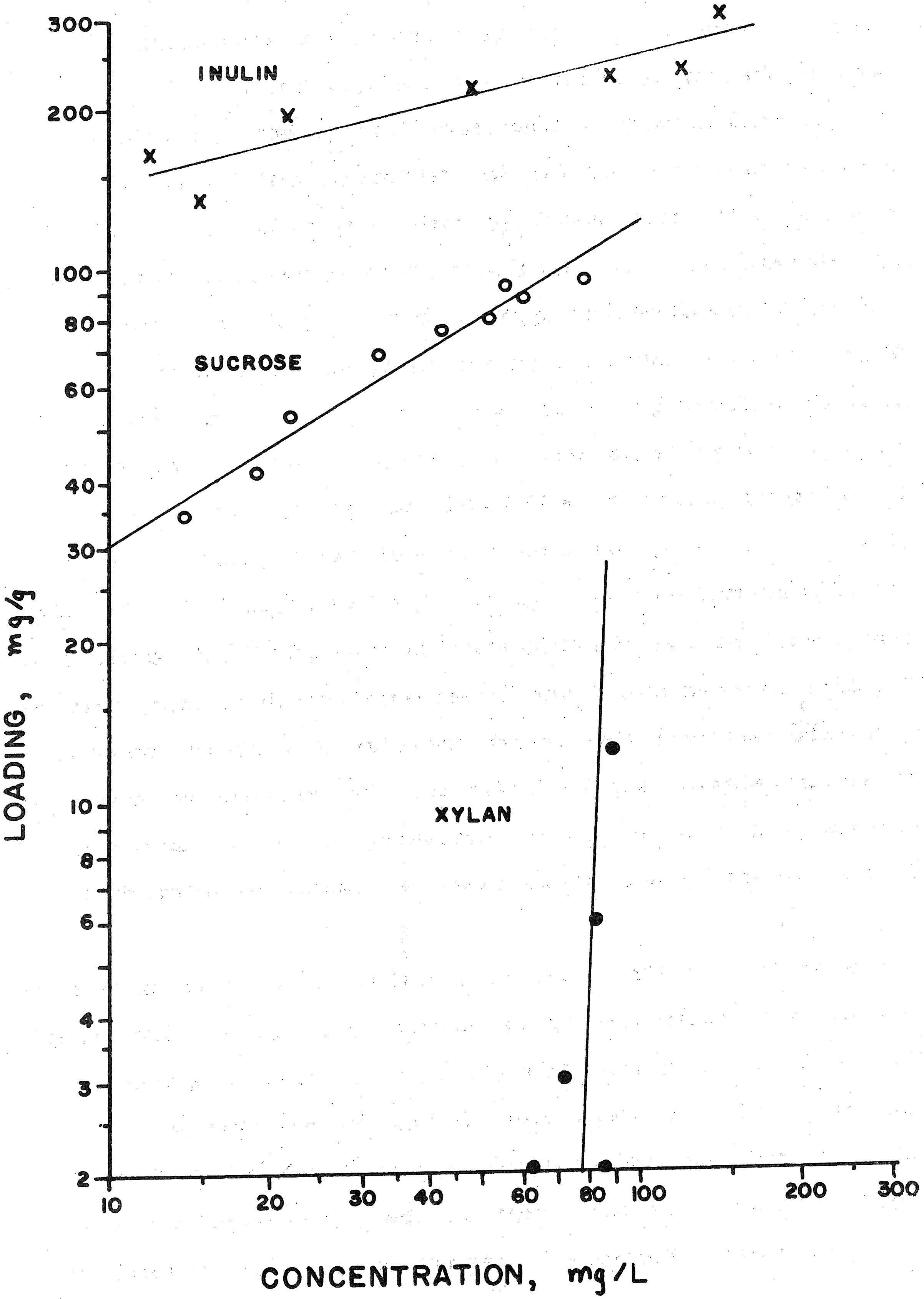

FIGURE 6: ISOTHERMS ON BAC-SQ

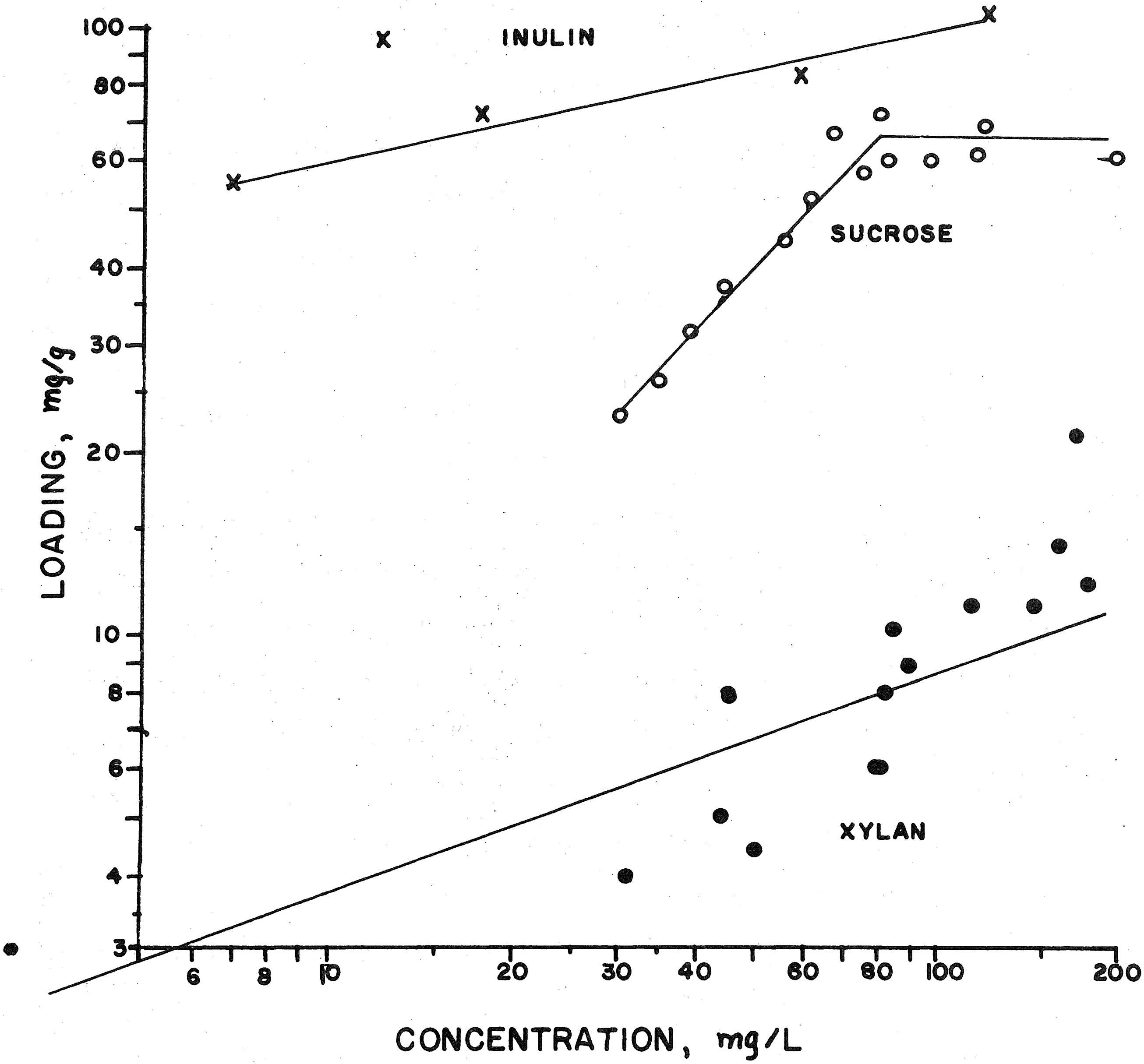

FIGURE 7: ISOTHERMS ON F400

with a low adsorptive capacity (maximum loading about 20 mg/g). F400 has more surface area and pore volume in the pores greater than 2 nanometers than BAC-SQ (53% versus 33%), permitting the larger molecule to penetrate somewhat into the adsorbent.

The adsorption pattern for the polysaccharides on HD4000 is slightly different than for other adsorbents (Figure 8). Inulin adsorption is again the best adsorbed compound, with a maximum observed capacity of 180 mg/g. But, xylan adsorbs better than sucrose on HD4000. This results from a combination of the relatively good adsorption of xylan (maximum loading of 36 mg/g) and the poor loading of the sucrose (maximum loading of 28 mg/g). The large pore structure of the HD4000 does not provide sufficient pore volume in the micropores for strong adsorption of small molecules, while providing larger pores for stronger xylan adsorption. Unlike the study with polyethylene glycols (44), a maximum capacity was obtained with this lignite carbon, and adsorbing larger similar molecules resulted in a lower loading; therefore, high loadings are not necessarily expected from the large-pored carbons.

The adsorption of additional large compounds was evaluated on F400: PEG - polyethylene glycol 400 (MW 400), PAA - polyacrylic acid (MW 5000), PVP - polyvinyl pyrollidone (MW 10,000), and albumin (MW 45,000) (Figure 9). As with the xylan on BAC-SQ, the albumin was poorly adsorbed, with a vertical isotherm near the starting solution concentration; its large size prevented any appreciable adsorption. The PEG is favorably adsorbed, with a Freundlich n of 3.89; adsorptive capacity at 100 mg/L equilibrium concentration was about 130 mg/g or considerably

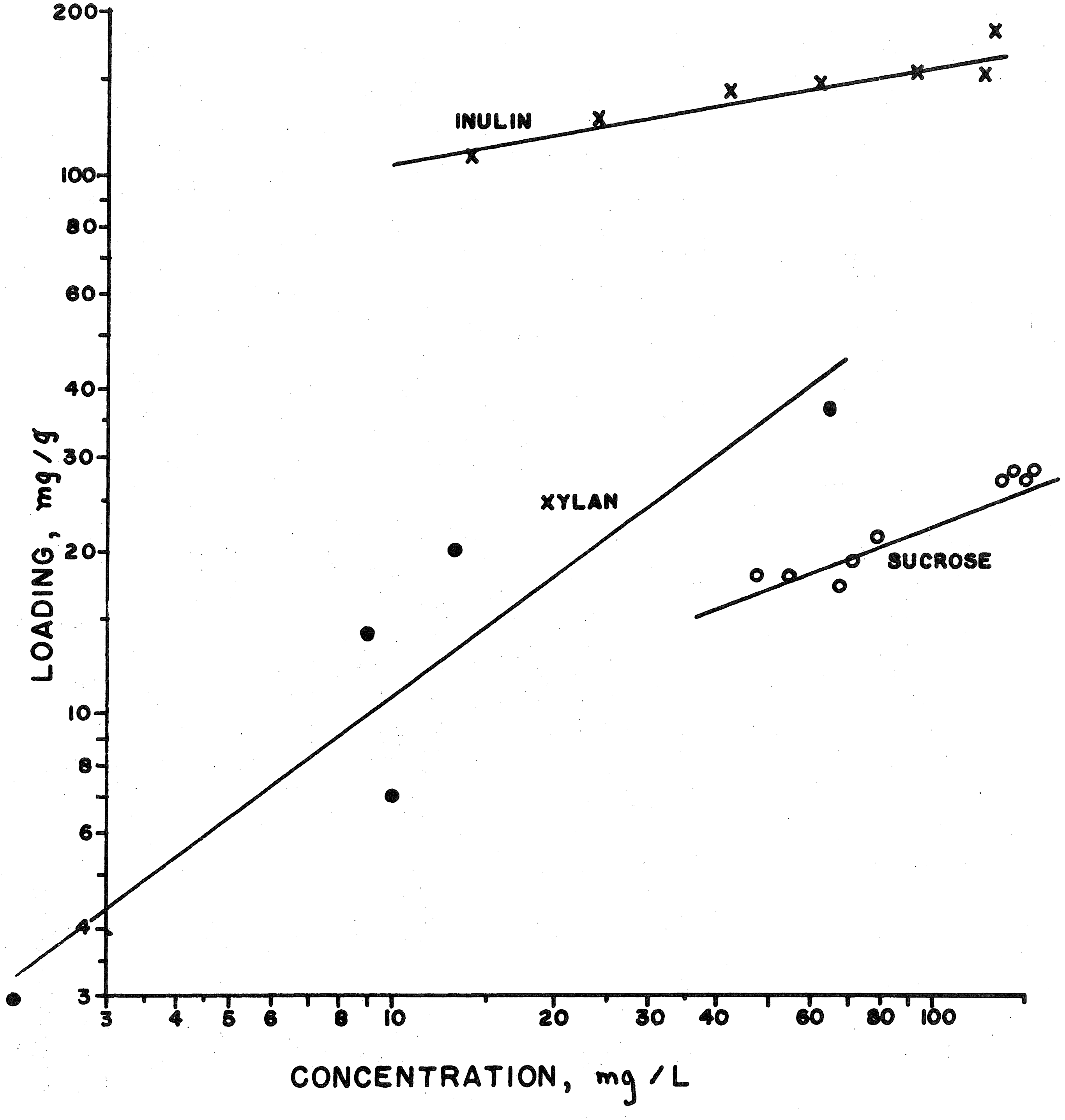

FIGURE 8: ISOTHERMS ON HD4000

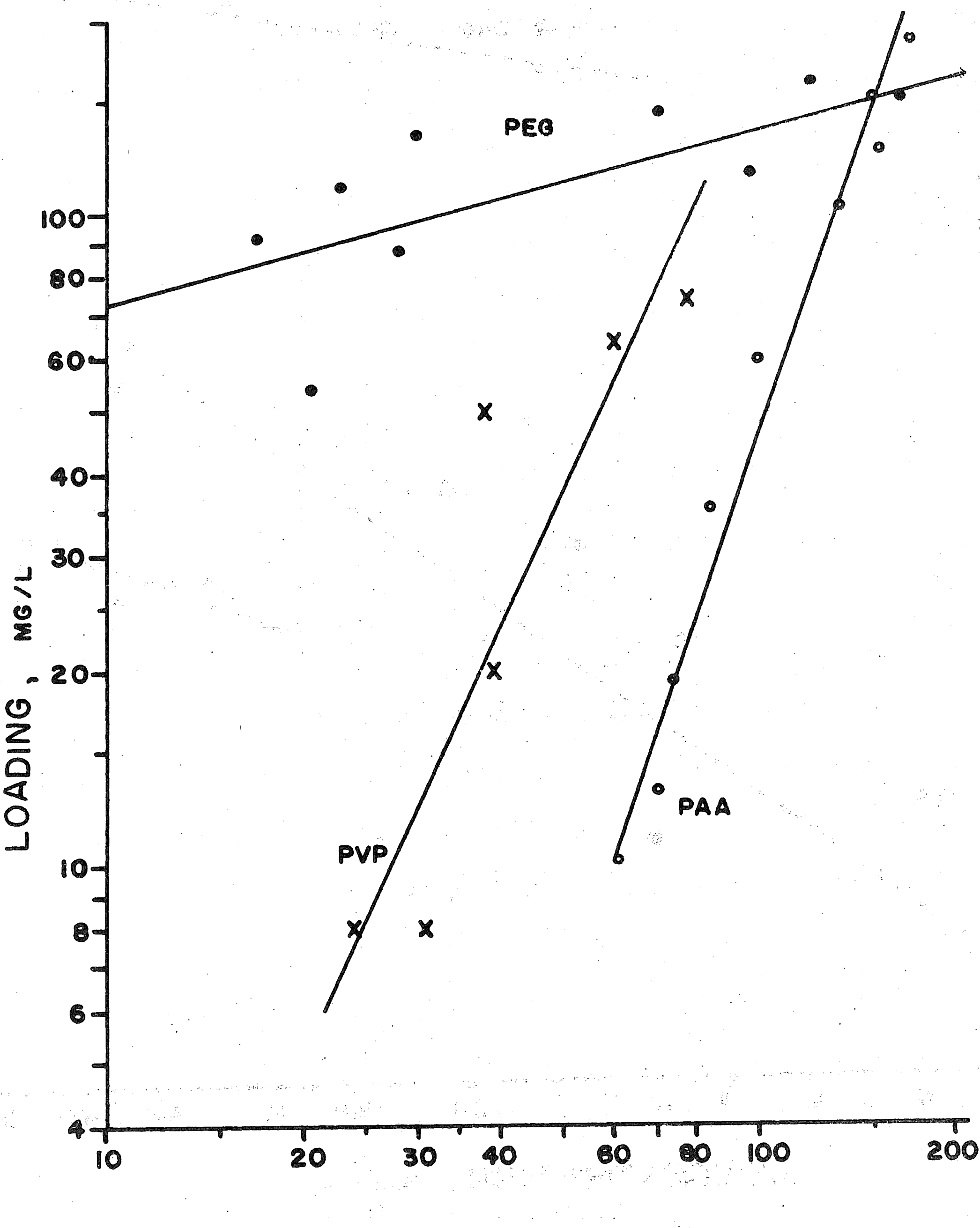

FIGURE 9: MISCELLANEOUS COMPOUNDS ON F400

greater than for sucrose's capacity of 66 mg/g at a similar concentration for the similarly sized compounds. So other factors in addition to size are important to its adsorption, as is the case for smaller compounds frequently studied. Adsorption of the 5000 MW PAA is unfavorable, with an n of .34; surface charge groups on the PAA must be an important consideration since this compound is not adsorbed in a manner similar to the comparably sized inulin. The PVP adsorption pattern is also unfavorable (n = .52), although the large compound's adsorption is reasonably good (64 mg/g) at an equilibrium concentration of 60 mg/L. The larger PVP adsorbs better than the PAA, with its capacity somewhat lower than the smaller inulin molecule, but considerably greater than the larger xylan molecule. The upper limit of the capacity obtained for the various large compounds tested except for the PAA, indicates that the optimum size for utilization of the F400 pore volume is about 5000, with either decreasing or increasing compound size resulting in lower adsorptive capacities. Note: a limited number of compounds from different families were studied, and very large concentrations were not tested to determine the actual limiting adsorptive capacities. A more extensive study of large compound adsorption is needed.

Column Tests:

The column studies were intended to monitor the breakthrough pattern of three different molecular weight materials to determine if size fractionation occurs within an adsorber. If molecular weight size fractionation occurred, it was to be determined if the smaller compound is able to displace the larger compounds and result in chromatographic effects, similar to those observed when small compounds are competing for adsorption sites (55). The three compounds included inulin, a polysaccharide that can be measured by the phenol-sulfuric acid test (48), phenol, which could be measured by ultraviolet spectroscopy, and polyethylene glycol (either 1000 or 14,000 molecular weight), which would be determined by total carbon -- the total organic carbon response of the equivalent amount of phenol and inulin would be subtracted from the sample's TOC, with the remaining TOC converted to PEG. Each compound was present at 75 mg/L. Four flows (0.5, 1, 2, & 4 gpm/ft2) were to be used to determine the superficial velocity and/or contact time effect on the breakthrough pattern.

While the program appeared reasonable and should have given insight into large compound adsorption, several problems developed. First, the principal investigator left the University of Florida in the middle of the project and the remaining funds could not be transfered to his new university. Second, the graduate student working on the equilibrium portion was replaced for the column studies, and a student was employed who was not dependent upon the study results for his graduation; the principal investigator therefore had little control over the remainder of the project. Third, several problems were encountered with the total organic carbon analyzer and the backup total organic carbon analyzer (Beckman 914), and the funds were not available to repair either system. Fourth, when the difficulty with the TOC analysis persisted, the samples were not shipped, as requested, to the principal investigator's new university so the TOC analyses could be performed (too much time may have transpired anyway). Therefore, the results presented here do not include three component interactions within the column, since only two were analyzed.

The breakthrough pattern for phenol and inulin at 1 gpm/ft2 flow with PEG 1000 indicates that inulin breaks through before phenol for the first and second columns (empty bed contact times of 7.5, and 15 minutes) (Figure 10); this could be predicted from Freundlich K values, since phenol's K is 78 and inulin's is 37 mg/g (55). But, when the phenol reached the third column, little capacity remained for it, while the inulin continued to be removed (contact time may have a significant effect on adsorption results, but more data are needed). Around day eight when the inulin broke through, a very steep breakthrough pattern was obtained, with its effluent concentration exceeding phenol's within two days. After 16 days, the fourth bed was still removing nearly all the phenol, with a relatively constant leakage of 3 to 4 mg/L of inulin. The PEG 1000 was expected to adsorb well, with its capacity likely to be greater than phenol's. How it breaks through the columns is not known, and its effect on the phenol's reversal of order in column three is not known; premature exhaustion may be occurring, but similar results would have been expected in the fourth column.

The 1 gpm/ft2 run using the PEG 14,000 results in inulin breaking through prior to the inulin in all three columns (Figure 11); the fourth column had to be removed from operation early in

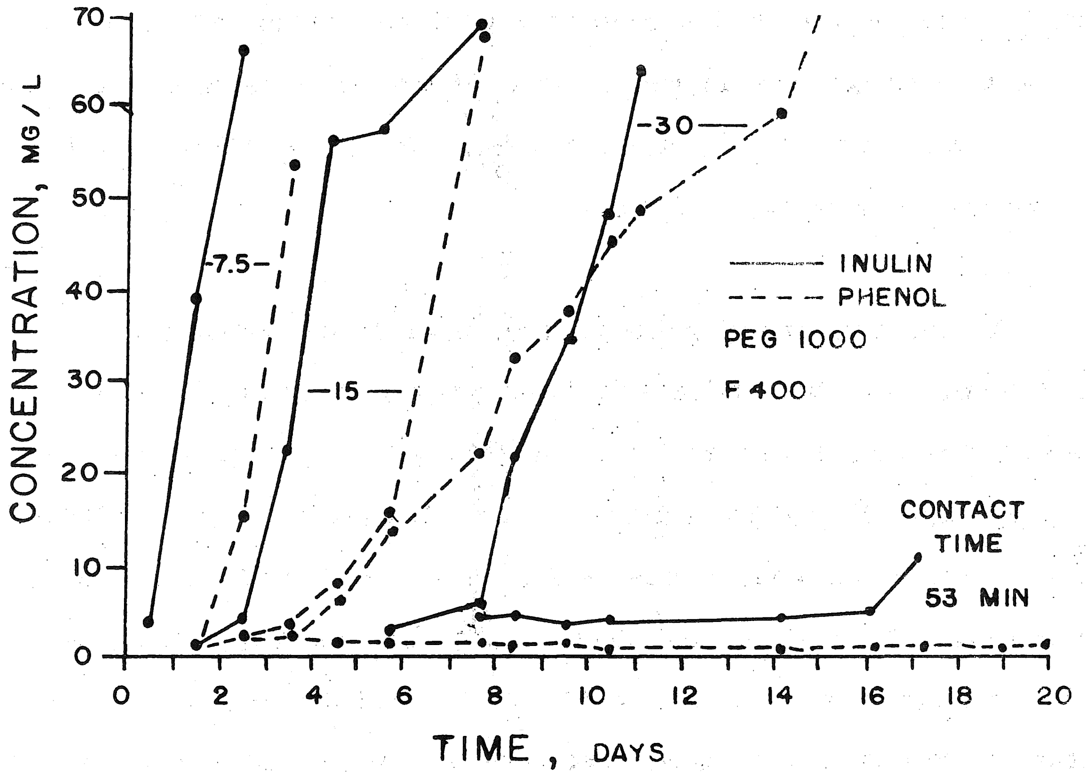

FIGURE 10: BREAKTHROUGH CURVES FOR 1 GPM/FT^2, PEG1000 SYSTEM

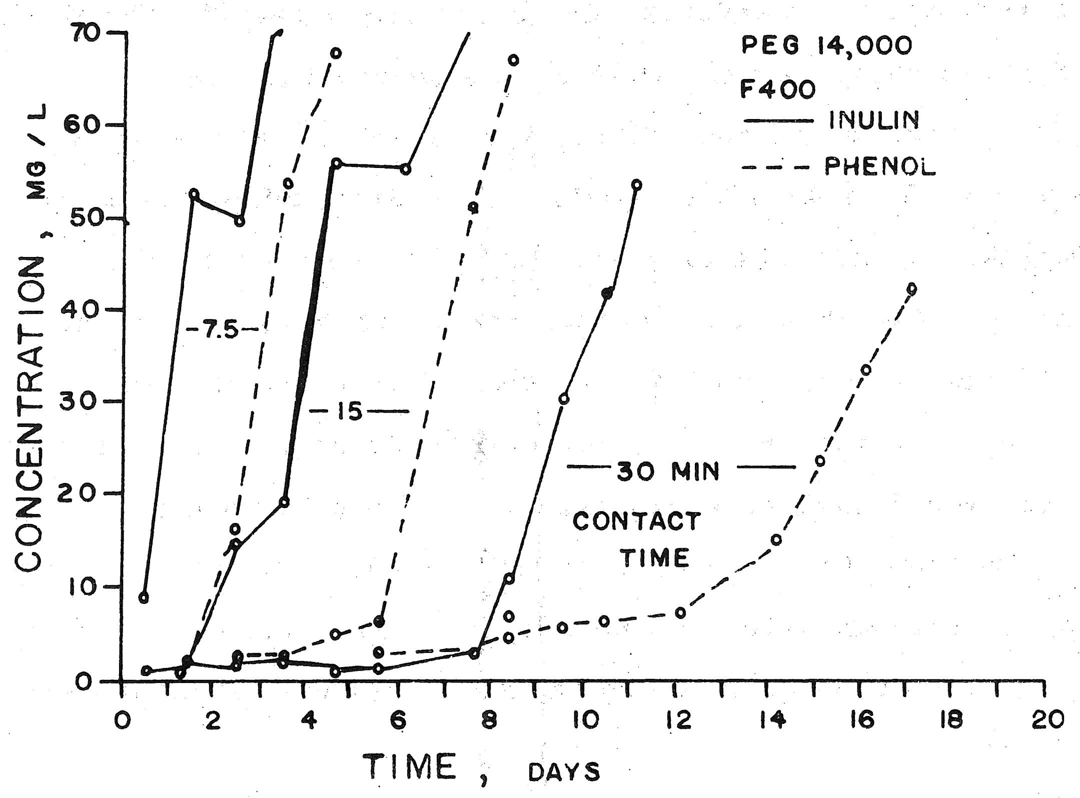

FIGURE 11: BREAKTHROUGH CURVES FOR 1 GPM/FT^2 SYSTEM

the run due to a rapid headloss buildup. The carbon's capacity for PEG 14,000 is expected to be less than for the phenol and inulin due to its larger size; whether it did remains to be determined. Times to breakthrough for both phenol and inulin are given for the two systems (Table III). PEG size had no effect on inulin breakthrough, even though the one PEG was smaller (MW = 1000, inulin = 5200) and the other was larger (MW = 14,000).

TABLE III

Times to Breakpoint
1 gpm/ft2 System

Compound	Breakpoint mg/L	Contact Time, min	Time, days PEG 1000	PEG 14,000
Inulin	10	7.5	.7	.5
		15	2.8	2.2
		30	7.9	8.3
	20	7.5	1.0	.7
		15	3.4	3.5
		30	8.3	8.9
	30	7.5	1.2	1.0
		15	3.7	3.8
		30	9.2	9.5
phenol	10	7.5	2.2	2.1
		15	4.9	5.8
		30	5.2	12.2
	20	7.5	2.6	2.6
		15	5.9	6.3
		30	7.3	14.7
	30	7.5	2.9	2.8
		15	6.3	6.7
		30	8.3	15.7

This indicates that both PEGs are better or more poorly adsorbed than the inulin, since the inulin apparently is seeing the same number of adsorption sites within the columns. With phenol, a difference is noted in the breakthrough pattern of the phenol. At the greater contact times, the phenol competes better for adsorption sites in the system with the higher MW PEG; this indicates that the larger PEG is not adsorbing as well as the smaller one at deeper locations in the adsorber. When the phenol reaches these points the adsorbent still has plenty of adsorption sites left for the phenol. Or conversely, all the larger PEG could be adsorbing on the same carbon already loaded with phenol and then the phenol doesn't have to compete for adsorption sites with the smaller PEG for sites; the first hypothesis is more likely due to kinetic considerations.

The same two chemical systems were evaluated at 2.0 gpm/ft2 (Figures 11 & 12). Again, the inulin breaks through the adsorbers before the phenol, in fact it has broken through the 7.5 minute empty bed contact time column before the phenol has broken through the 3.75 minute columns. Breakthrough for both the phenol and the inulin is rapid, with less than a day needed from the time breakthrough begins. The times to different breakpoints were determined for the different PEGs (Table IV).

The different PEGs have no apparent effect on either phenol or inulin breakthrough at this higher superficial velocity, and longer contact times were not tested.

At 4 gpm/ft2, the headloss was too great for our system and within three days the runs were abandoned with the 7.5 minute contact time systems performing the same for both PEGs. The 0.5 gpm/ft2 runs were not performed, and therefore the longer contact times were not tested. The greatest effects of flow rate were expected to be observed at the slowest flow and greatest contact

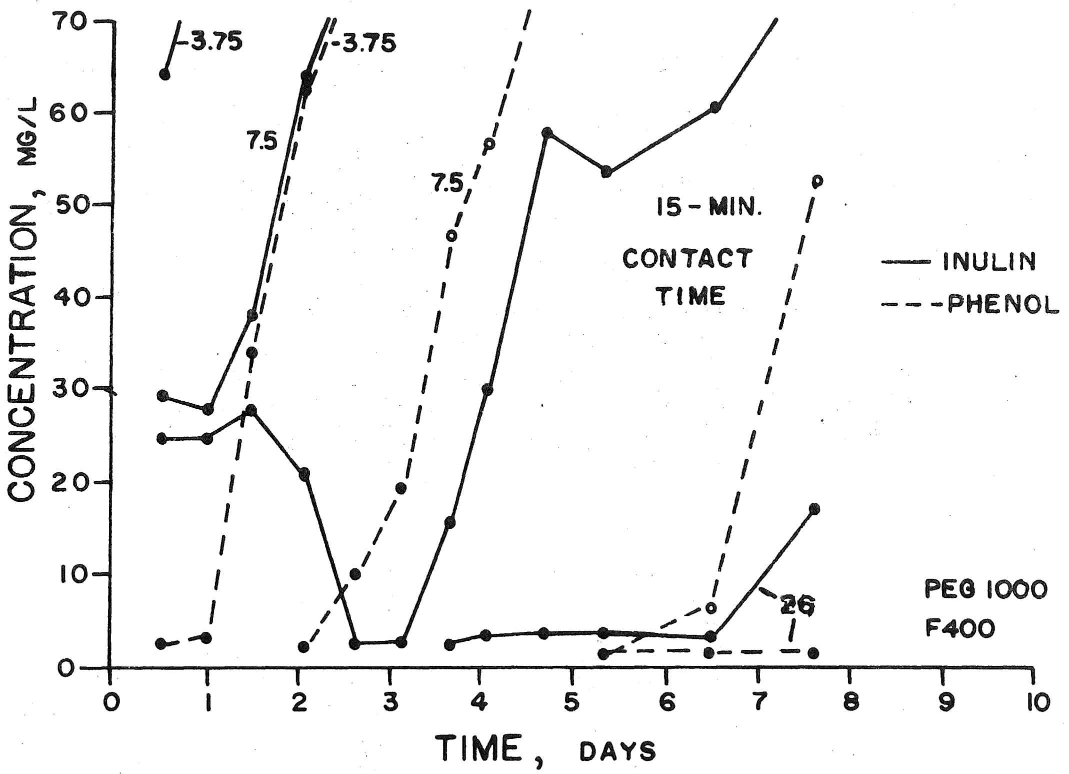

FIGURE 12: BREAKTHROUGH CURVES FOR 2 GPM/FT^2 SYSTEM, PEG 1000

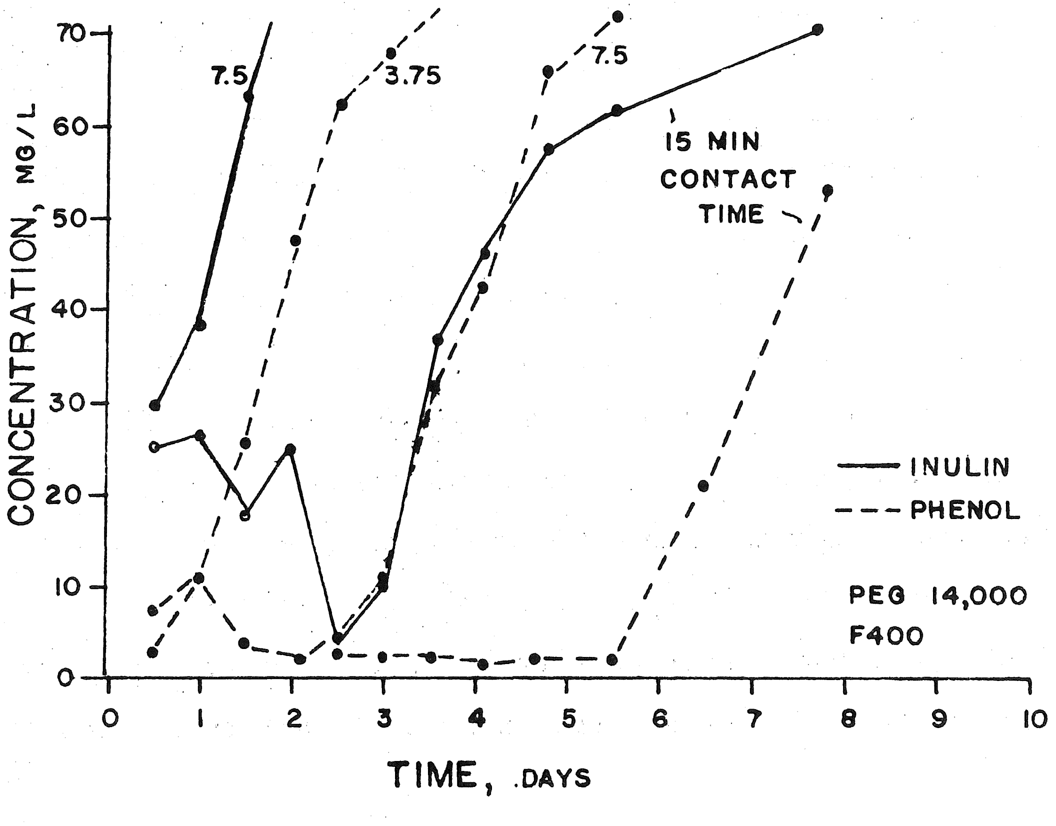

FIGURE 13: BREAKTHROUGH CURVES FOR 2 GPM/FT^2 SYSTEM, PEG 14000

time, since it was under similar conditions that the premature breakthrough was observed (40).

TABLE IV

Times to Breakpoint
2 gpm/ft2 system

Compound	Breakpoint mg/L	Contact Time, min	Breakthrough Time, days	
			PEG 1000	PEG 14,000
Inulin	10	15	3.4	3.1
	20	15	3.8	3.3
	30	7.5	1.1	.6
		15	4.1	3.4
phenol	10	3.75	1.1	.9
		7.5	2.6	3.0
		15	6.6	6.4
	20	3.75	1.3	.9
		7.5	3.1	2.9
		15	6.8	6.8
	30	3.75	1.5	1.6
		7.5	3.3	3.6
		15	7.1	7.1

Activated carbon use rates were calculated to the 30 mg/L breakpoint of both phenol and inulin for the several contact times at each flow (Figure 14). With inulin, little difference in carbon usage is observed between the PEG 1000 (solid line) and the 14,000 (dashed line) at all contact times when the flow is 1 gpm/ft2; but, when the flow is 2 gpm/ft2, a substantial difference was observed at the 7.5 minute contact time. The larger PEG caused the inulin to breakthrough much faster, increasing the carbon usage; whether the inulin moved with the PEG or the PEG blocked the adsorption sites is unknown. Phenol

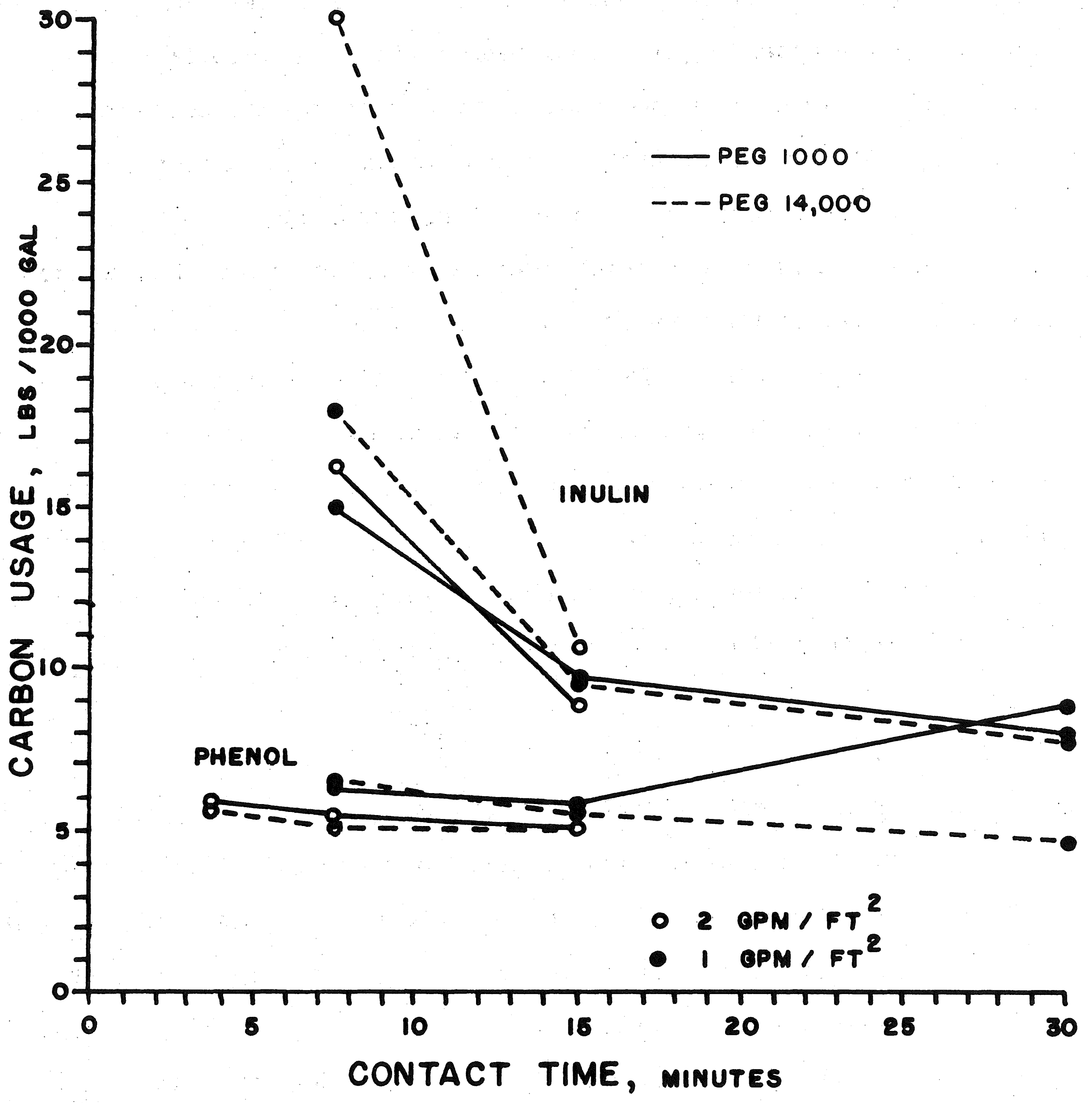

FIGURE 14: CARBON USAGE TO A 30 MG/L BREAKPOINT

breakthrough is unaffected by the PEG at the 2 gpm/ft2, but at the 30 minute contact time with the 1 gpm/ft2, premature breakthrough is possibly observed with the smaller PEG. The smaller PEG probably proceeded deeper into the adsorber and blocked the pores as hypothesized in the premature breakthrough article (19). More contact time studies need to be performed as well as determination of the PEG breakthrough.

Contact time has a significant effect on the carbon usage for the larger inulin molecule, with contact times less than 15 minutes causing substantially greater carbon usages (Figure 14). The carbon usage for phenol breakthrough is not affected considerably by contact time, except in the case for the smaller PEG at the long contact time. So in the case of one molecule, longer contact times are needed for better removal, while for the smaller molecule this may prove detrimental.

CONCLUSIONS

1. The 5200 MW polysaccharide (inulin) adsorbed much better on all three adsorbents than did the 342 MW sucrose or the 20,000 MW xylan, as is evidenced by both the Freundlich isotherm adsorption energy term (K constant) and the adsorption intensity term (n).
2. A small-pored acitvated carbon (BAC-SQ) has little adsorption space for large MW compounds (20,000 MW).
3. Even for the large-pore activated carbon (HD4000), pore volume accessibility is limited, since xylan (20,000 MW) capacity is much less than for inulin (5200 MW), unlike when adsorbing a series of PEGs.

4. No chromatographic effect was noted for phenol or inulin in column runs at 1 or 2 gpm/ft2 with either PEG.
5. Inulin breaks through the column before phenol at both flows, as would be expected from the Freundlich K values.
6. Carbon use decreases with increased contact time for inulin in both flow systems.
7. Carbon use decreases with increased contact time for phenol at 2 gpm/ft2 for both PEG systems.
8. Premature exhaustion may occur at longer contact times (30 minutes) at 1 gpm/ft2, since carbon use increased for the PEG 1000 system.

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