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ADSORPTION OF ORGANIC COMPOUNDS ONTO SOLIDS FROM AQUEOUS SOLUTIONS

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PREFACE

The use of solids to remove pollutants is not novel in the sense that solids are used presently for this purpose. For example, the use of charcoal is well known, and the use of alumina in phosphate removal has been investigated. The removal of phenol from aqueous solutions on a variety of solids has been studied in this work. The rationale for this study is as follows. An aqueous solution containing a pollutant (phenol) is a three component system consisting of a solute (phenol) and solvent (water) in contact with a solid. The question arises, what about the removal of the pollutant by the solid? In many instances the kinds of solids that have been used are those which not only compete for the pollutant, but also compete for water. Thus, not only is the interaction between the pollutant and the solid important, but also the interaction between the water and the solid. In many systems, for example herbicides, insecticides, and phenol, there is a limited solute concentration, which means that there is a basic incompatability in the system to start with. Then as this solution is put in contact with a solid surface, the amount of pollutant and the amount of water removed become relevant. If the solid has an attraction for water in addition to the pollutant, water may be removed and block parts of the solid which could be effective in removing the pollutant. This study has been concerned with the adsorption of phenol from aqueous solutions on several solids chosen to alter the competition of water and phenol for the surface of the solid.

The authors would like to acknowledge the contributions to this work of Miss A. Burton and Mr. R. K. Lengel.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

The removal of pollutants by adsorption at solid surfaces is a specific example of adsorption from solution. Solution adsorption is a complex process involving, in part, competition of all components for the solid surface. The role of the surface energy of the solid in the competitive adsorption process has not been studied systematically. The system phenol-water-solid was chosen in this study since phenol is a commonly encountered pollutant. It is well known that surfaces vary in surface energy as gauged by hydrophilicity, that is, the affinity of the surface for water. For example, silica is very hydrophilic, whereas Teflon is hydrophobic. Thus, when considering adsorption from solution, changes in the surface energy of the solid can alter the affinity of water for such surfaces. Charcoal, a well-known adsorbent, is partially hydrophilic to varying extents depending upon preparation and pretreatment. Solids with less affinity for water than charcoal are of interest. Polymers represent such a class of solids. The surface areas of these materials are generally low and hence the amount of pollutant removed on a unit weight basis is smaller than on charcoal. However, there may be a compensating effect of a diminished affinity for water. Polymers have seldom been studied as adsorbents although the use of polymers is widespread.

The purpose of this research was to study the adsorption of phenol from aqueous solutions on solids varying in surface energy. Particular emphasis was placed on the use of polymers as adsorbents. The amount of phenol adsorbed on silica, carbon, Nylon, polyethylene, and Teflon was measured over a wide range of concentrations. The temperature dependence of adsorption was established in the case of carbon. The solids were characterized by surface area measurements, infrared spectra, and contact angle measurements to better define the factors effecting phenol adsorption.

EXPERIMENTAL PROCEDURES

Characteristics of the powdered solids used in the several phases of this study are listed in Table 1. Many solution adsorption studies reported in the literature deal only with the determination of the amount of material adsorbed. One of the major objectives of this study was the characterization of the solids used as adsorbents. Contact angles were measured and infrared spectra were obtained, in addition to the surface areas, for the six solids used.

TABLE 1

SAMPLE CHARACTERISTICS AND SURFACE AREAS

Type	Name	Lot No.	Supplier	Surface Area (m^2/gm)
Silica	Cab-O-Sil	–	Cabot	223. (N_2)
Carbon	Graphon	–	Cabot	87. (N_2)
Nylon	Aviamide-6	CRD-9455	FMC Corp.	1.5 (Kr)
Polyethylene	Microthene FN-510	–	Gulf	0.35 (Kr)
	Alathon	810253	DuPont	0.10 (Kr)
Teflon	Teflon-6	10295	DuPont	8.5 (N_2)

Surface Areas

The surface areas of the solids were measured using a conventional BET apparatus[1] employing either nitrogen or krypton as the adsorbate. The solid samples were outgassed to an ultimate pressure of $< 1 \times 10^{-5}$ Torr at room temperature prior to the determination of surface area. A computer program was used for data reduction.

Contact Angles

The critical surface tensions of the polymers (Alathon, Microthene, and Teflon) were obtained from contact angle measurements. It was not possible to obtain contact angles on either Cab-O-Sil, Graphon, or Aviamide.

Materials The solids (listed in Table 1) used to prepare the substrates on which contact angle measurements were made were all obtained in powdered form. Each sample was prepared for contact angle measurements in the way described below. Microthene and Alathon were melted against a Teflon surface on one side and against a glass slide on the other. Slight pressure was applied to the glass slide as the polymer was melting. The side melted against the glass was used in measurement. Teflon was prepared by compression into pellets. This was done by applying a pressure of 1000 psi to 50 mg of Teflon for five minutes in a Carver Laboratory Hydraulic Press.

All pellets, except Teflon, prepared with the Carver Laboratory Hydraulic Press absorbed the contact angle liquids, thereby preventing contact angle measurements.

An unsuccessful attempt was made to melt Aviamide. Aviamide was pressed, using the hydraulic press, into pellets that appeared satisfactory; however, when the contact angle liquid was applied, the pellet exploded. Therefore, it could not be used in contact angle determinations.

The six standard contact angle liquids were purified as described below.

Water - Distilled water was redistilled from an alkaline $KMnO_4$ solution. The reflux column was packed with glass beads.

Glycerol - Fisher U.S.P. glycerol was vacuum-distilled at 38 Torr and the fraction boiling at 197 to 198°C was collected.

Formamide - Fisher reagent grade formamide was vacuum-distilled at 40 Torr and the fraction boiling at 107 to 109°C was collected and stored in an aluminum covered glass bottle.

Aniline - Fisher certified A.C.S. aniline was vacuum-distilled at 47 Torr and the fraction boiling at 90 to 91°C was collected and stored in an aluminum covered glass bottle.

Bromobenzene - Fisher reagent grade bromobenzene was stirred overnight with 10 percent KOH solution twice, washed with redistilled water, and dried over P_2O_5. The resulting bromobenzene was vacuum-distilled twice at 638 Torr and the fraction boiling at 119 to 120°C was collected and stored in an aluminum covered glass bottle.

Ethylene Glycol - Fisher certified ethylene glycol was distilled at 476 Torr and the fraction boiling off at 155 to 156°C was collected.

All of the purified liquids were stored in tightly stoppered glass bottles and aliquots were removed with a syringe from beneath the surface of the liquid.

Surface tension, as determined by the capillary rise method, was used to check the purity of each liquid. In the capillary rise method, the height a liquid will rise in a capillary tube is used to determine the surface tension of the liquid. The defining equation is

$$\gamma_{LV} = \tfrac{1}{2}hdgr,$$

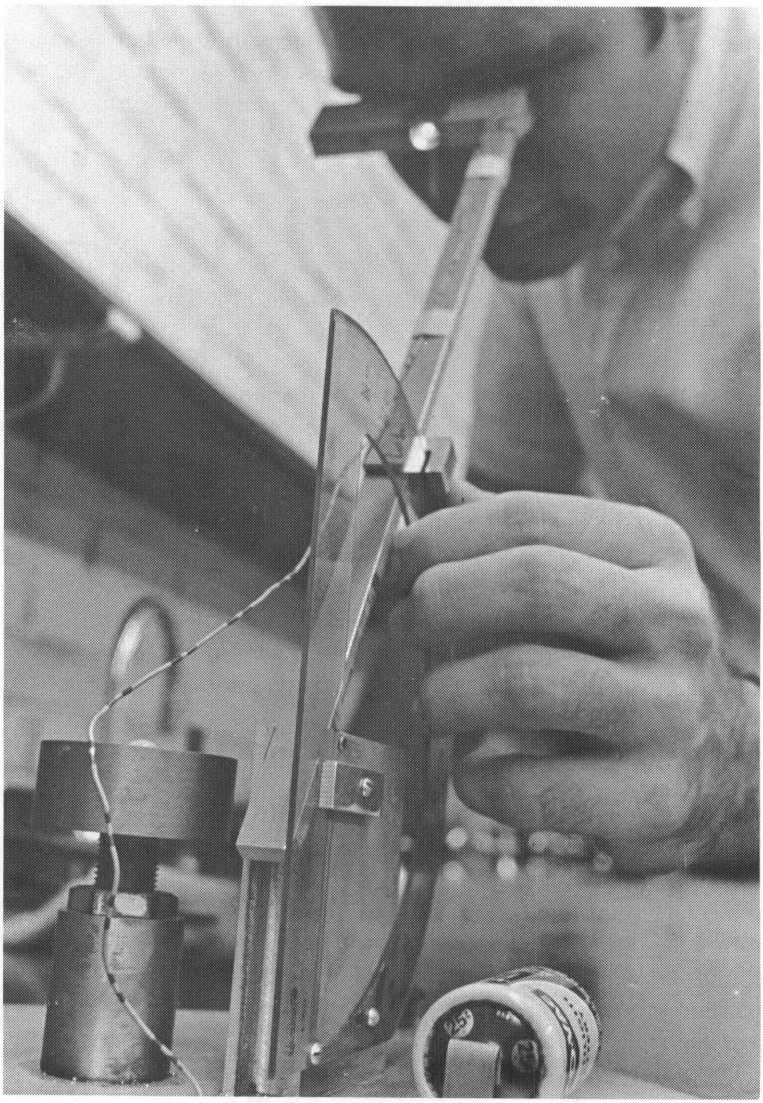
where γ_{LV} is the surface tension of the liquid, h is the height of the rise of the liquid of density d, in a capillary of radius r, and g is the gravitational constant.

The capillary tube used was a broken thermometer cleaned with hot, concentrated nitric acid. The capillary tube was held by a two-hole rubber stopper, which also held a small piece of glass tubing. When the stopper was placed in an 8-inch test tube which held the liquid of which the surface tension was to be determined, the glass tubing was used to apply pressure or to create a slight vacuum in the test tube. This was done in order to reach the point of equilibrium from both the top and the bottom of the capillary. The radius of the capillary was determined from the equation above, using water as the calibrating liquid of known surface tension. Methylene iodide and bromonaphthalene were discarded as standard contact angle liquids because the surface tension obtained experimentally did not correspond closely enough to the literature values.

Procedure Contact angle measurements were made by employing two different methods. The first method involved use of a goniometer.[2] A drop was placed on the solid substrate which was mounted on the pedestal of the goniometer. The drop was exposed to the atmosphere. The second method involved the use of the Gaertner M204 eyepiece and a microscope. The solid substrate on which the contact angle liquid was placed was mounted on a glass slide supported by a ring stand. A glass box was placed over the solid substrate and the contact angle liquid in order to maintain vapor-liquid equilibrium.

An Industrial and Scientific Instrument Co. syringe (5cc) was used to apply the contact angle liquid in both methods used. Formation of advancing

MEASURING CONTACT ANGLE WITH GONIOMETER.
NOTE LIQUID DROP RESTING ON STAGE AT LEFT.



contact angles was accomplished by carefully applying small drops of liquid from the syringe until the drop on the solid substrate approached a diameter of 2 to 3 mm. After the drop was formed, five minutes was allowed for the drop to reach equilibrium. Three contact angle measurements were made for each solid-liquid combination. A fresh polymer sample was used for each measurement.

A series of aqueous phenol solutions of varying concentrations from 0.12 to 9.1 weight percent phenol were also used as a set of liquids to make contact angle measurements. The procedure for these measurements was the same as described above for the pure liquid.

Infrared Spectra

The identification of chemical constituents present in the solids (listed in Table 1) was done by multiple internal reflection (MIR) infrared spectroscopy. It was not possible to obtain the infrared spectra of Graphon.

Procedure: Sample Preparation The infrared spectra were obtained when the sample was either in a pellet form or in the original powdered form. Three techniques were used in pellet preparation and two techniques were used in which the sample was powdered. The pelletized samples were melted, pressed alone, and/or pressed with KBr. The powdered sample was applied to the Wilks Multiple Internal Reflection (MIR) KRS-5 crystal by directly sprinkling onto both faces of the crystal and mounting in either an unfixed or fixed plate sample holder.

The melts of the samples were accomplished in one of the following three ways whenever a melt was possible: In technique A, the sample was sprinkled on a glass slide, melted on a standard hot plate, cooled, and peeled off. In technique B, a second glass slide was used to flatten the sample before melting, but was removed before the melt began. In technique C, the sample was melted between two slides, with slight external pressure applied during the melt. The quality of the pellets prepared by the above methods is shown in Table 2.

TABLE 2

QUALITY OF PELLETS PRODUCED BY SEVERAL METHODS

Sample	MELTS			PRESS		
	A	B	C	Mini-Press (Pure)	Hydraulic Press (Pure)	Mini-Press (KBr)
Microthene FN-510	S	E		S		S
Alathon		S	E		S	S
Cab-O-Sil					S	S
Aviamide-6						S
Teflon-6				E		S

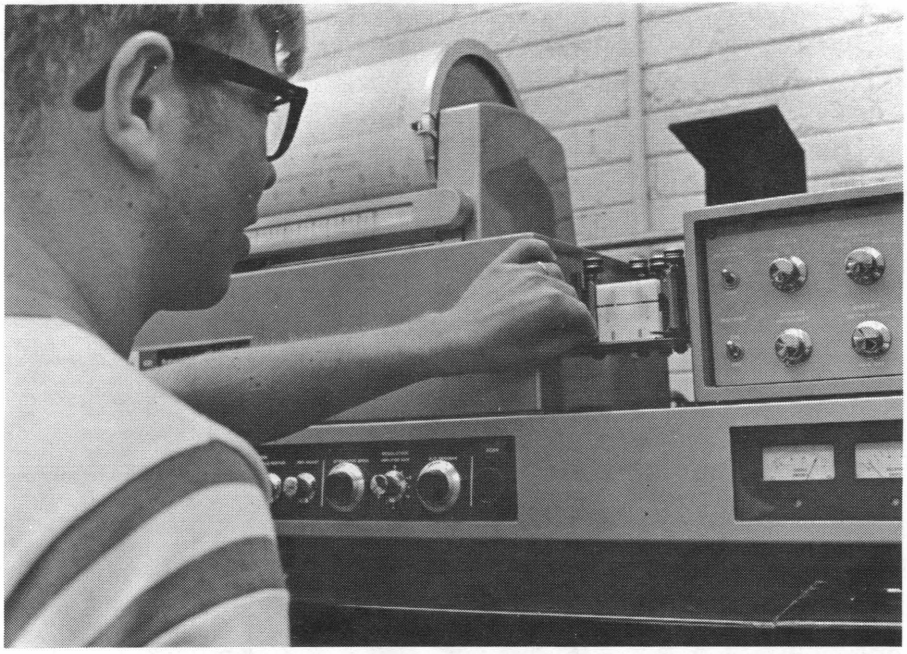
S - Satisfactory E - Excellent

Pellets were attempted for all samples on two presses: the Wilks Mini-Press and the Carver Laboratory Hydraulic Press. The amount of sample and the pressure were not recorded for the Wilks Mini-Press, but the press time was one minute for each sample. No improvement was noted for fifteen minutes press time. The amount of sample and the pressure were varied, but the press time remained at five minutes for the hydraulic press samples. The quality of the pellets prepared in this manner is shown in Table 2.

The KBr pellet technique involved the use of the Wilks Mini-Press. The pressure was applied for one minute, and the sample mixture consisted of one hundred milligrams of KBr and one milligram of sample. The quality of the KBr pellets is shown in Table 2.

The amount of sample sprinkled on the KRS-5 crystal was not recorded for the MIR infrared spectra. However, both faces of the crystal were completely covered with the powdered sample. The use of Scotch tape to hold the sample on the crystal proved unsatisfactory, since absorptions due to the tape were observed.

ADJUSTING INFRARED TRANSMISSION ON REFLECTANCE ATTACHMENT.



Procedure: Spectra All spectra were obtained on the Perkin Elmer 621 spectrophotometer. Two Wilks sample holders were used interchangeably. The fixed plate holder, Wilks Model MIR-29, was preferable to the solid sample holder, Wilks Model MIR-2. Both used the KRS-5 crystal, differing only in the size of the crystal. Both holders attached to the Wilks Model 9 Single Beam Internal Reflection Attachment, which in turn attached to the spectrophotometer.

Two sets of spectra were obtained differing in the ordinate scale expansion. One set of spectra was obtained at a scale of one (1X), while the second set was obtained at a scale expansion ten times the first (10X). The instrument settings for the two cases were those recommended by the manufacturer.

Reference spectra were obtained for a pure KBr pellet and the KRS-5 crystal at both scale expansions. Checks were performed on the KRS-5 crystal throughout the work to check percent transmission which is indicative of crystal face contamination. These checks were made with the KRS-5 crystal in a Wilks Teflon calibration holder. The KRS-5 crystal is too badly scratched to be used if the percent transmission of the crystal falls significantly lower than the values of a fresh crystal listed in Table 3.

TABLE 3

TRANSMISSION CHARACTERISTICS OF KRS-5 CRYSTALS

MIR-2		MIR-29	
Angle of Attack	% Transm.	Angle of Attack	% Transm.
30°	27	30°	25
45°	17	45°	18
60°	10	60°	11

The MIR spectra were compared with the KRS-5 reference spectra to determine those peaks characteristic of the sample. The MIR spectra were then compared with the spectra of the melted or pressed samples where the powders were destroyed, to determine those peaks characteristic of the bulk

sample. Any remaining peaks in the MIR spectra can be attributed to surface functional groups present on the powder. The spectra obtained with KBr pellets were used to supplement the MIR spectra.

Phenol Adsorption

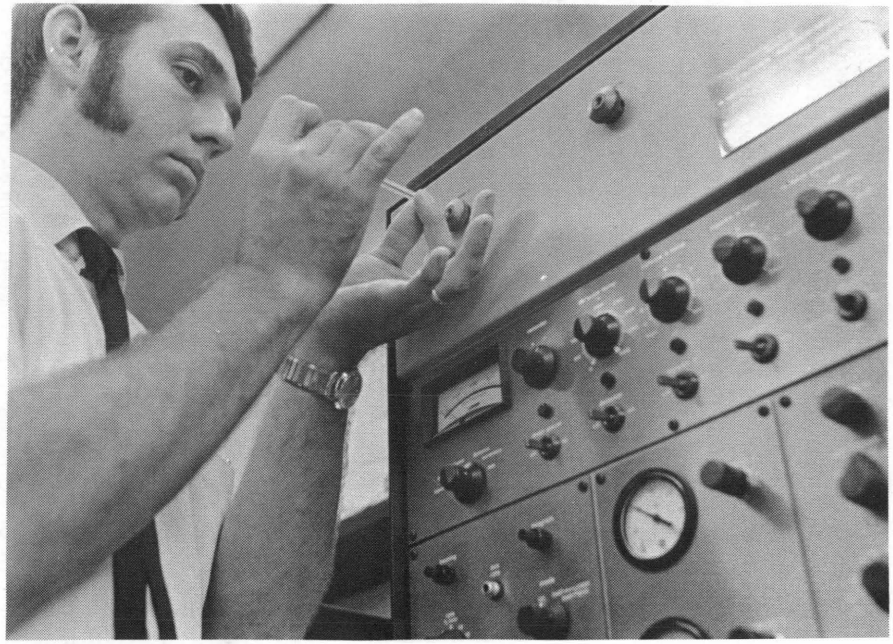
The amount of phenol adsorbed from aqueous solutions at 25°C onto a given solid was determined from measured changes in phenol concentration after equilibration with the solid.

Phenol Preparation The phenol was prepared by distillation of a commercial laboratory grade of phenol under a nitrogen atmosphere. The phenol contained H_3PO_2 as a preservative. The first and last fractions of the distillation were discarded and the fraction to be used was stored in a freezer under a nitrogen atmosphere. A series of fifteen aqueous phenol solutions were made in 100 gm quantities. Water and phenol were weighed with an Ohaus "Cent-O-Gram" triple beam balance to ± 0.01 gm and with a Sartorius single arm balance to ± 0.01 mg, respectively. The concentration range of the series was from 0.1 to 9.0 weight percent phenol.

Procedure and Analysis The adsorption series were prepared by placing a known quantity of solid and a known quantity of the above solutions into custom glass ampoules. These ampoules were fire sealed and the neck of the ampoule was broken just prior to injection into the gas chromatograph. The sealed glass ampoules were not conducive to multiple sampling. Glass vials, sealed with crimped butyl rubber seals, were also used in this study. In the test of system reliability, three 15-tube series were prepared. Prior to chromatographic analysis of the phenol solution in contact with a given solid, a sample of the original solution was injected into the chromatograph in order to calibrate the hydrogen flame-detector/recorder-disk integrator. The standard solutions were stored in a freezer to maintain quality and were brought to the same equilibrium temperature as the test sample shortly before the analysis of the series. The test samples were equilibrated for a minimum of 48 hours in a constant temperature rocker water bath which maintained the temperature in a range of ± 0.1 degree C.

Since 70 to 90 injections were performed for each series of 15 test samples and calibration samples, the strain on the chromatograph septum and on the delicate syringe used to inject one microliter was severe. The best configuration found was the stacking of two three-layer composite Hamilton septums and the use of one microliter Scientific Glass Engineering syringe.

INJECTING PHENOL SAMPLE INTO GAS CHROMATOGRAPH.



The septums consist of a soft, pliable sealing layer of silicone rubber sandwiched between two thin layers of more elastic rubber which resists crumbling and helps maintain the integrity of the inner layer. The syringe is designed with the plunger traveling the full length of the needle barrel and has the capacity of one microliter. The syringe may be disassembled and working parts may be replaced. Another convenient feature contributing to the syringe's reliability is the replaceable Teflon seal which ensures reproducible displacement of the solution in the needle barrel.

A Varian Aerograph Series 1700 gas chromatograph was used to measure the concentration of phenol. The column used was one meter in length and loaded with 12 percent by weight SE-30 on 30/60 mesh Teflon 6. The column was prepared in this laboratory by dissolving SE-30 in methylene chloride and mixing the SE-30 solution with Teflon 6 particles. Upon evaporation of the methylene chloride, the coated particles were chilled in a freezer and packed in a ¼-inch OD aluminum tubing. The column was operated at 165°C under 7.5 psi of helium. The injection port and detector were operated at 195°C with an electrometer current of 10^{-9} amp. The peaks were integrated by a ball and disk integrator on a Sargeant Model SR recorder. The full scale error of the integrator was found to be 4 percent.

EXPERIMENTAL RESULTS AND DISCUSSION

Surface Areas

The surface area of each powdered solid determined from low temperature nitrogen or krypton adsorption are listed in the last column of Table 1. Note that the polymers, as contrasted to Cab-O-Sil and Graphon, are characterized by significantly lower surface areas. This fact has limited the use of polymers as adsorbents in adsorption studies.[3] On the other hand, one of the objectives of this study was the use of polymers to determine if a low surface area necessarily results in a low adsorption capacity of phenol.

Contact Angles

The results of surface tension determinations of the liquids used in the contact angle measurements are shown in Table 4. The observed values were corrected to 20°C and compared with the literature values for each liquid. The results of the contact angle measurements are discussed separately for each polymer.

TABLE 4

SURFACE TENSIONS OF TEST LIQUIDS

Liquid	γ_{LV} (dyne/cm) at 20°C	
	Observed	Literature[4]
Water	–	72.8
Glycerol	63.7	63.4
Formamide	59.1	58.2
Ethylene glycol	48.7	47.7
Aniline	41.0	42.9
Bromobenzene	36.7	36.5

Microthene FN-510 Measured contact angles of the test liquids on Microthene are shown in Table 5. The cosine of the contact angle is shown as a function of the surface tension of the liquids in Figure 1. The critical surface tension (γ_c) obtained by extrapolation to zero contact angle ($\cos \Theta = 1$) through three points was 35 ergs/cm^2.

TABLE 5

CONTACT ANGLES OF TEST LIQUIDS ON POLYMERS

Liquid	Run No. 1	2	3	4	Avg.	γ_c (ergs/cm^2)
		MICROTHENE				35.
Water	83°	87°	82°	80°	83°	
Glycerol	67	89	74	82	78	
Formamide	69	82	67	76	74	
Ethylene Glycol	69	62	67	63	65	
Aniline	49	41	53	48	48	
Bromobenzene	28	(9)	20	28	25	
		ALATHON				31.5
Water	89°	89°	88°	90°	89°	
Glycerol	88	89	(78)	88	88	
Formamide	80	80	86	90	84	
Ethylene Glycol	72	72	72	77	73	
Aniline	41	44	43	40	42	
Bromobenzene	27	24	38	28	29	
		TEFLON				28.
Water	99°	106°	99°	–	101°	
Glycerol	81	88	92	–	87	
Formamide	90	79	81	–	83	
Ethylene Glycol	71	77	73	–	74	
Aniline	61	65	57	–	61	
Bromobenzene	42	39	44	–	42	

The contact angle on Microthene was also determined as a function of the concentration of the aqueous phenol solution as shown in Figure 2. A smaller contact angle is observed for solutions of higher phenol concentration.

FIGURE 1

WETTABILITY OF MICROTHENE FN-510 BY VARIOUS LIQUIDS.

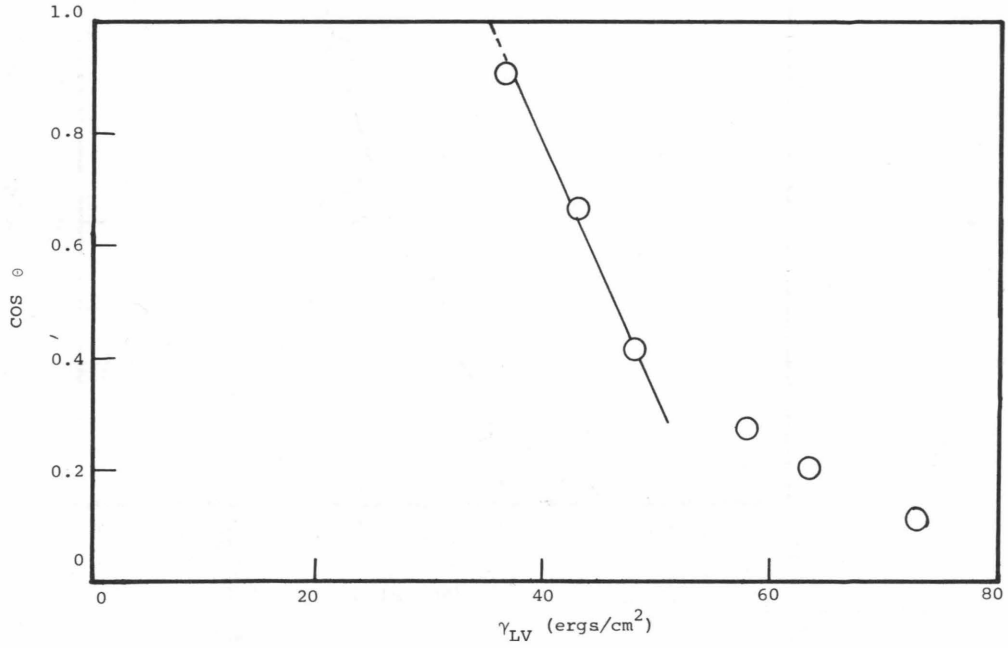
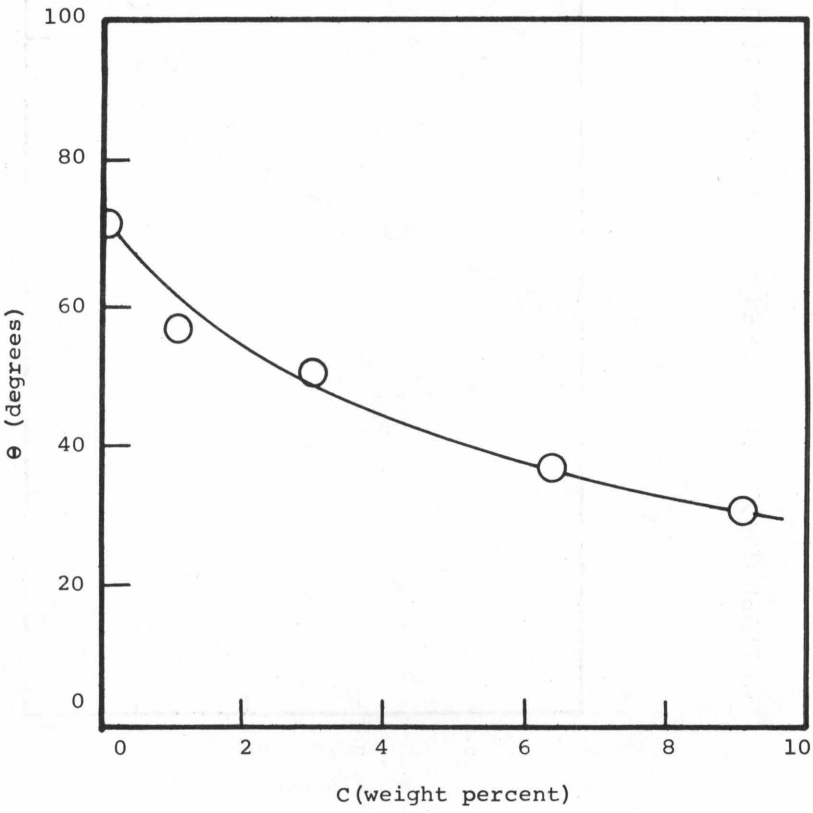


FIGURE 2

CONTACT ANGLE (Θ) VS. CONCENTRATION
(C, WEIGHT PERCENT) OF PHENOL SOLUTIONS
ON MICROTHENE FN-510.



Alathon Measured contact angles of the test liquids on Alathon are shown in Table 5. The cosine of the contact angle is shown as a function of the surface tension of the liquids in Figure 3. The critical surface tension obtained by extrapolation to zero contact angle ($\cos \Theta = 1$) through four points was 31.5 ergs/cm^2. The correspondence of the critical surface tensions of Microthene and Alathon is not surprising since both solids are polyethylenes. Zisman[5] gives a value of 31 ergs/cm^2 for the γ_c value of polyethylene.

The contact angle is plotted as a function of the concentration of the aqueous phenol solutions in Figure 4. The contact angles for any given phenol solution are significantly higher on Alathon than on Microthene except for the highest concentration. The higher contact angles on Alathon are consistent with its lower value of the critical surface tension, γ_c.

Teflon Measured contact angles of the test liquids on Teflon are shown in Table 5. The cosine of the contact angle is shown as a function of the surface tension of the liquids in Figure 5. The critical surface tension obtained by extrapolation to zero contact angle ($\cos \Theta = 1$) was 28 dyne/cm which is significantly higher than the 18 dyne/cm reported in the literature.[5] No rationale is offered for the discrepancy.

The contact angle is plotted as a function of the concentration of the aqueous phenol solutions in Figure 6. The shape of the curve is similar to those observed for the other polymers. On the other hand, the contact angle is significantly higher on Teflon for any given phenol concentration.

Infrared Spectra

The infrared spectra of the solids studied are discussed below for each solid. It was necessary to obtain the spectrum of KBr used as a matrix in the transmission technique and the spectrum of the KRS-5 crystal (a thallium bromide-thallium iodide mixture) used in the reflection technique at scale expansions of X1 and X10. Absorptions due to these materials were subtracted totally from the appropriate spectra of the solids studied.

Silica Cab-O-Sil is a flame-hydrolyzed silica. The MIR spectra of Cab-O-Sil at scale expansions of X1 and X10 were obtained and also the transmission spectrum of Cab-O-Sil in a KBr matrix at a scale expansion of X10. The major absorption bands of Cab-O-Sil obtained from the above spectra are listed in Table 6. The wavenumber of the band is given in the first column. Observance

FIGURE 3

WETTABILITY OF ALATHON BY VARIOUS LIQUIDS.

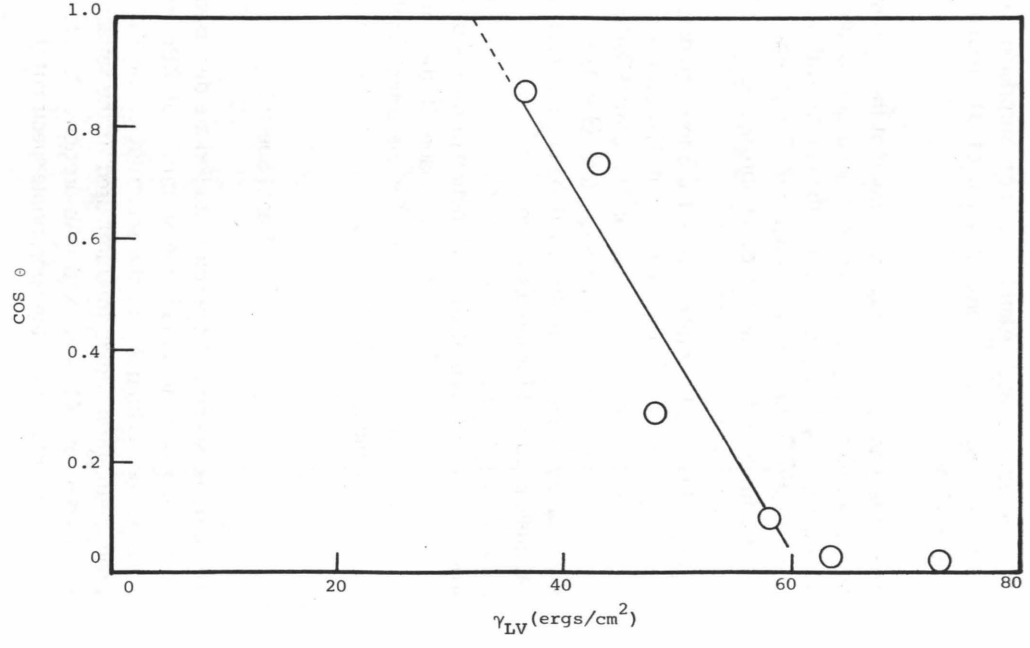


FIGURE 4

CONTACT ANGLE (Θ) VS. CONCENTRATION
(C, WEIGHT PERCENT) OF PHENOL SOLUTIONS
ON ALATHON.

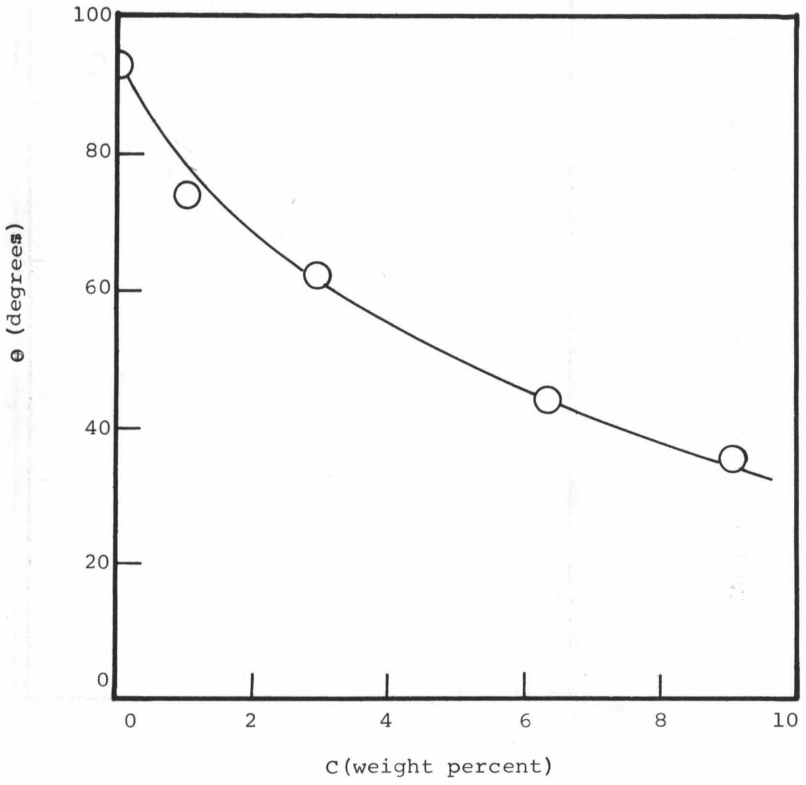


FIGURE 5

WETTABILITY OF TEFLON BY VARIOUS LIQUIDS.

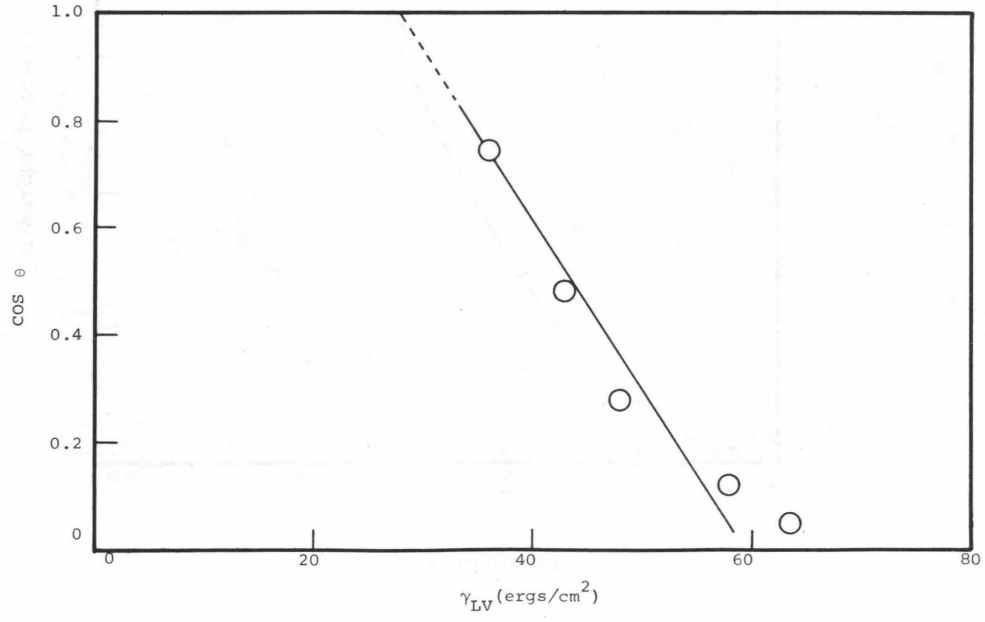
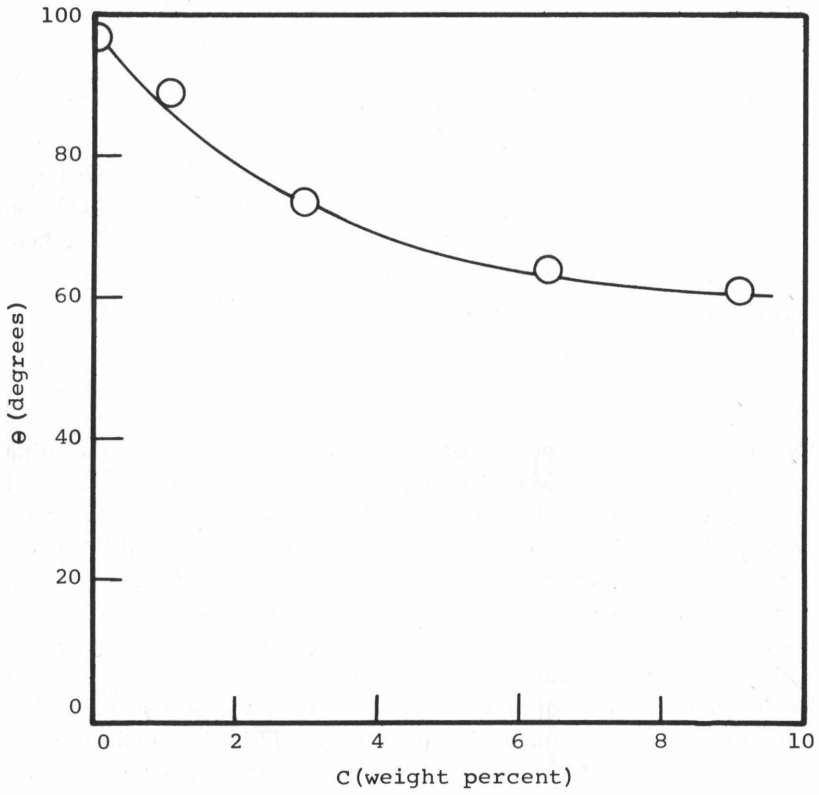


FIGURE 6

CONTACT ANGLE (Θ) VS. CONCENTRATION
(C, WEIGHT PERCENT) OF PHENOL SOLUTIONS
ON TEFLON.



of the band in the MIR spectra at scale expansions of X1 and X10 is indicated by an (X) in the next two columns. The provisional assignment of the band is given in the last column. The peaks at 1100 and 800 cm^{-1} are due to Si-O vibrations. The peaks at 3250 and 1640 cm^{-1} are due to O-H vibrations either from surface silanol (Si-OH) groups or from water physisorbed on the silica surface.

TABLE 6

PROVISIONAL ASSIGNMENTS OF ABSORPTION BANDS OF CAB-O-SIL

Wavenumber (cm^{-1})	MIR (X1) No. 26-3	MIR (X10) No. 34-5	Assignment
3250		X	O-H stretch
1640		X	O-H bend
1100	X[a]	X[b]	Si-O stretch
800	X[a]	X[b]	Si-O bend

[a]present also in KBr (X1) matrix

[b]present also in KBr (X10) matrix

Nylon-6 Aviamide samples were not available at the time the infrared spectra were run. However, since Aviamide is basically Nylon-6, it was felt that the spectra of Gulf Nylon-6 would be representative of the ir spectra of Aviamide. The MIR spectra of Nylon-6 at scale expansions of X1 and X10 were obtained, and a comparison of these two spectra illustrated the necessity of having the scale expansion capability when doing ir spectra of materials where the detection of limited concentrations is important. Weak or absent peaks at a scale expansion of X1 were clearly observed at X10. The transmission spectrum of Nylon-6 in a KBr matrix at a scale expansion of X10 was obtained. The major absorption bands of Nylon-6 obtained from the above spectra are listed in Table 7. Peaks characteristic of the bulk sample appear at 3300, 2920, 2850, 1630, 1525, 1450, 1255, and 800 cm^{-1}. The other peaks may be due to groups on the Nylon-6 surface or to groups present in small concentration in the bulk Nylon-6. It was not possible to obtain a melted sample of Nylon-6, hence no further differentiation of the two types of groups was possible.

TABLE 7

PROVISIONAL ASSIGNMENTS OF ABSORPTION BANDS OF NYLON-6

Wavenumber (cm^{-1})	MIR (X1) No. 26-1	MIR (X10) No. 31-2	Assignment[6,7]
3300	X	X	(N-H) stretch
3080		X	(N-H) stretch
2920	X	X	(C-H) stretch (-CH_2)
2850	X	X	(C-H) stretch (-CH_2)
1630	X	X	(C=O) stretch
1525	X	X	(N-H) bend
1450	X	X	(C-H) bend (-CH_2-)
1370		X	(C-H) bend
1255	X	X	(CH_2) twist
1235		X	(CH_2) wag
1200		X	(NH) vib
1165		X	(NH) vib
1070		X	(C-C) vib
800	X	X	(C-C) vib

Polyethylene Two polyethylenes, Microthene and Alathon were studied. The MIR spectra of Microthene at scale expansions of X1 and X10 were obtained as well as the transmission spectrum of Microthene in a KBr matrix. The MIR spectra of Alathon at scale expansions of X1 and X10 were obtained. The major absorption bands of these polyethylenes are listed in Table 8. The peaks at 2900, 2850, 1450, and 710-720 cm^{-1} represent absorption in bulk polyethylene. Microthene is characterized by a larger number of peaks in the X10 spectra than Alathon. This may be quite significant since a difference in contact angles of phenol solutions was observed between Microthene and Alathon. The peaks at 3100, 1500, 1190, and 1100 cm^{-1} in Microthene may be attributed to surface groups since they did not appear in the pressed sample which for polyethylene is equivalent to a melted sample. All the peaks in Alathon are attributed to bulk groups.

TABLE 8

PROVISIONAL ASSIGNMENTS OF ABSORPTION BANDS OF POLYETHYLENE

Wavenumber (cm^{-1})	MIR (X1) Microthene (No. 25-1)	MIR (X1) Alathon	MIR (X10) Microthene (No. 33-1)	MIR (X10) Alathon	Assignment[8]
3100			X		
2960			X[a]		(CH_3) stretch
2920				X[b]	
2900	X	X		X[b]	(CH_2) stretch
2850	X	X	X[a]	X[b]	(CH_2) stretch
1500			X		
1450	X	X	X[a]	X[b]	(CH_2) bend
1190			X		
1100			X		(CH_2) wag
710-20	X	X	X	X[b]	(CH_2) rock

[a]present also in pressed sample

[b]present also in melted sample

Teflon The MIR spectra of Teflon at scale expansions of X10 and X1 were obtained. The major absorption bands are listed in Table 9. The MIR (X1) spectra is very simple having only one intense peak at 1150-1200 cm^{-1}. The MIR (X10) spectra shows additional peaks, however, and the peaks at 1150-1200, 935, 780, and 715 cm^{-1} also appeared in a pressed sample hence the peak at 1300^{-1} cm indicates the presence of a surface group.

TABLE 9

PROVISIONAL ASSIGNMENTS OF ABSORPTION BANDS OF TEFLON

Wavenumber (cm^{-1})	MIR (X1) (No. 26-6)	MIR (X10) (No. 35-6)	Assignment[9,10]
1300		X	
1150-1200	X	X[a]	$(C\text{-}F_2)$ sym stretch
935		X[a]	(C-F) vib
780		X[a]	amorphous
715		X[a]	amorphous

[a]present also in pressed sample

Phenol Adsorption

The results of studies of adsorption of phenol from aqueous solutions at 25°C onto Cab-O-Sil, Graphon, Aviamide, Microthene, Alathon, and Teflon are shown in Table 11 to 16, respectively, in the Appendix. The Teflon used in the adsorption studies was also obtained from du Pont but had a surface area of 2.4 m^2/gm. Values of the reduced concentration (C/C_o), that is the ratio of the equilibrium concentration to the solubility of phenol in water at 25°C, are tabulated in the second column in each table. The range of reduced concentrations studied was 3×10^{-4} to 0.97. The amount of phenol adsorbed (ϕ), expressed in grams of phenol per gram of solid, is shown in the last column in each table.

The isotherm for the adsorption of phenol on Cab-O-Sil is shown in Figure 7 where ϕ is plotted against C/C_o. The data plotted in Figures 7 to 12 are taken from Tables 11 to 16 in the Appendix. The maximum at $C/C_o \sim 0.5$ may reflect competitive adsorption of both phenol and water at the polar silica surface.[11]

The isotherm for the adsorption of phenol on Graphon is shown in Figure 8. This isotherm compares favorably with isotherms reported by Hansen, Fu, and Bartell[12] for the adsorption of phenol on several types of carbons. For example, the amounts of phenol adsorbed per gram of adsorbent were 0.40 and 0.32 m-moles/g at a reduced concentration of ~0.08 for Hansen's and the present work, respectively. The comparison is only valid if made on the basis of nearly equivalent surface areas as is the case for Type A graphite and Graphon. The increase in ϕ at high reduced concentrations is characteristic of adsorption from partially miscible systems.[13] The phenol-water-Graphon system was the most extensively investigated both in terms of the amount of experimental data obtained (see Table 12) and the study of the temperature dependence of adsorption. There was no significant difference noted in adsorption at 20° and 30°C. It was concluded that the effect of temperature on the amount of phenol adsorbed on Graphon was negligible. This is in marked contrast to the sharp temperature dependence observed for adsorption of gases on solids.

The isotherm for the adsorption of phenol on Microthene is shown in Figure 9. There is noticeable scatter in the data compared to the two previous isotherms. The minimum in the isotherm at a reduced concentration of 0.50 may be real. Hansen and Craig[14] have reported a similar effect in the adsorption of an homologous series of fatty acids from aqueous solution on Spheron.

FIGURE 7

ADSORPTION OF PHENOL FROM AQUEOUS SOLUTION
ON CAB-O-SIL AT 25°C.

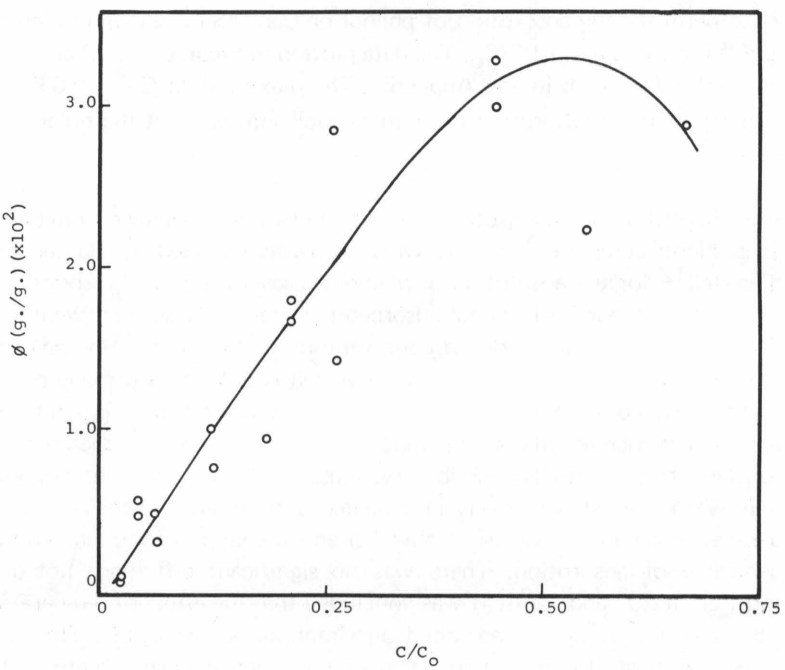


FIGURE 8

ADSORPTION OF PHENOL FROM AQUEOUS SOLUTION ON GRAPHON AT 25°C.

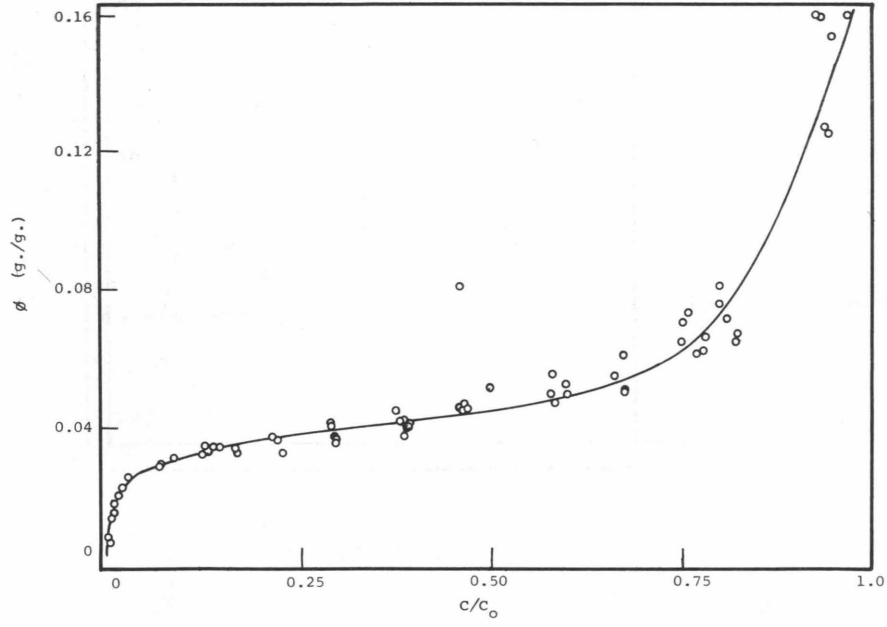
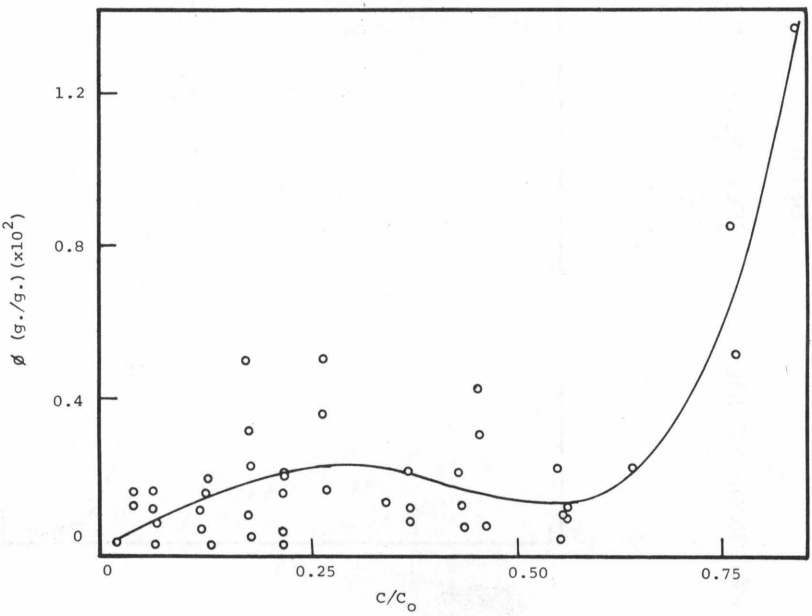


FIGURE 9

ADSORPTION OF PHENOL FROM AQUEOUS SOLUTION
ON MICROTHENE AT 25°C.



The isotherm for the adsorption of phenol on Alathon is shown in Figure 10. The minimum is not as well defined for Alathon as for Microthene in the previous isotherm.

The isotherm for the adsorption of phenol on Teflon is shown in Figure 11. The scatter is most pronounced for this case; however, as can be seen from the ordinate scale, the amount of phenol adsorbed is quite small. In fact, the limit of detection of the present gas chromatographic technique is approached.

Finally, the isotherm for the interaction of phenol with Aviamide is shown in Figure 12. Note the linear relationship between the quantity of phenol removed and the reduced concentration and also the reduced scatter, in this case, compared to the other three polymers. The copious quantities of phenol removed by Aviamide suggest a sorption process as contrasted to an adsorption process; that is, a solution (reaction) of phenol with the matrix of Aviamide rather than interacting solely at the surface. This is a significant result in that large quantities of phenol can be removed by use of Nylon polymers.

It should be emphasized that the curves shown in Figures 9, 10, 11, and 12 are unique in that these are some of the first isotherms reported for adsorption from solution on polymer surfaces.

A comparison of the phenol adsorption capacity of the various solids used is shown in Table 10. The order of adsorption on a unit weight basis as inferred from the results shown in column two is Aviamide $>$ Graphon $>$ Cab-O-Sil $\gg$ Alathon $\simeq$ Microthene $\simeq$ Teflon at a reduced concentration of 0.1. However, the comparison should be made on a unit surface area basis rather than a unit weight basis; that is, the number of molecules which can be adsorbed at a solid surface is determined in part by the surface area and not the weight of the solid. The surface areas were measured and have been noted in Table 1. Thus, the order of adsorption on a unit surface area basis is Aviamide $>$ Alathon $>$ Microthene $>$ Graphon $\simeq$ Teflon $>$ Cab-O-Sil at a reduced concentration of 0.1. This order is significantly different from the order obtained on a unit weight basis. Further, this order on a surface area basis would be expected considering the surface polarity of the solid, with the exception of Aviamide and Teflon. This is a significant result, and it has not been demonstrated previously. Polymers which usually have a low specific surface area can compete quite favorably with high specific area solids, for example, charcoal, in the removal of phenol from aqueous solution.

FIGURE 10

ADSORPTION OF PHENOL FROM AQUEOUS SOLUTION ON ALATHON AT 25°C.

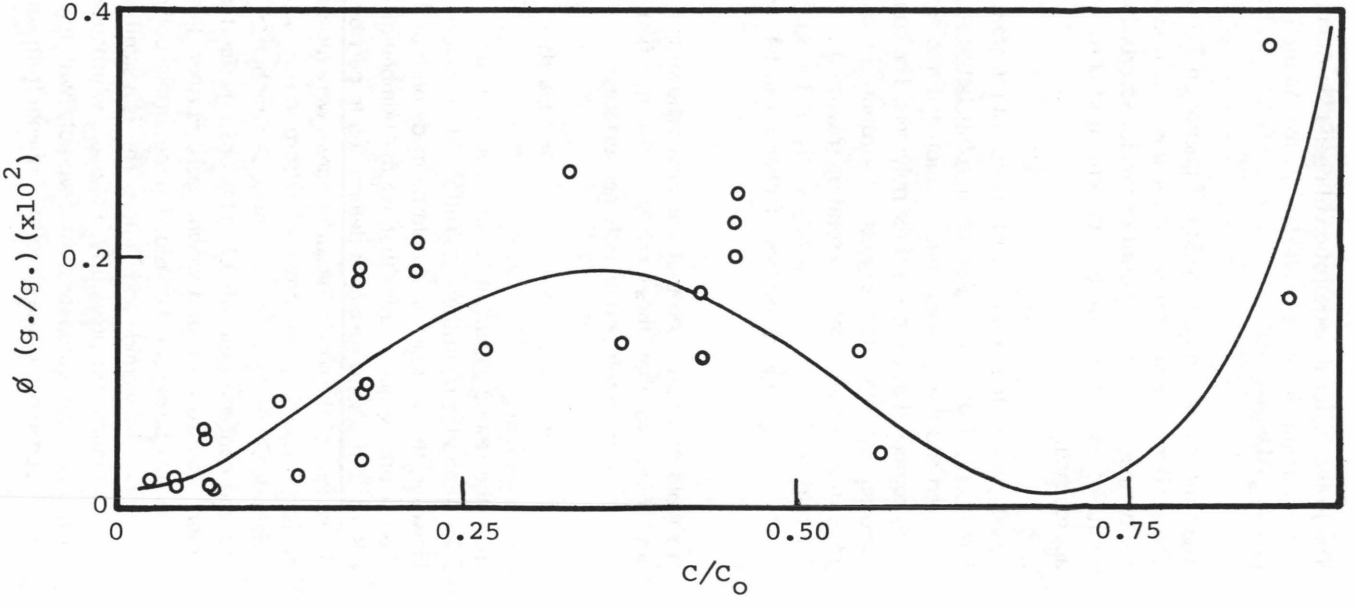


FIGURE 11

ADSORPTION OF PHENOL FROM AQUEOUS SOLUTION
ON TEFLON AT 25°C.

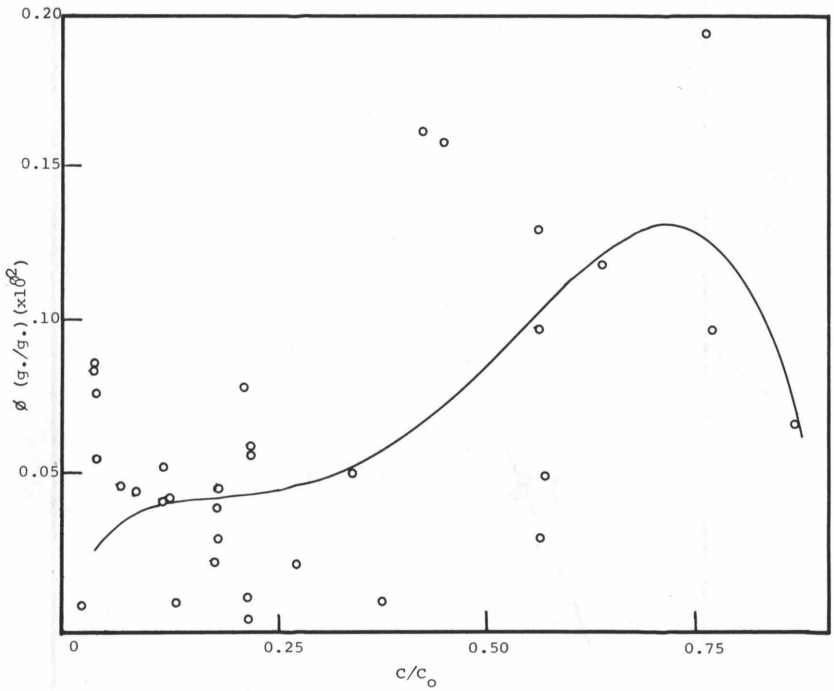


FIGURE 12

ADSORPTION OF PHENOL FROM AQUEOUS SOLUTION ON AVIAMIDE AT 25°C.

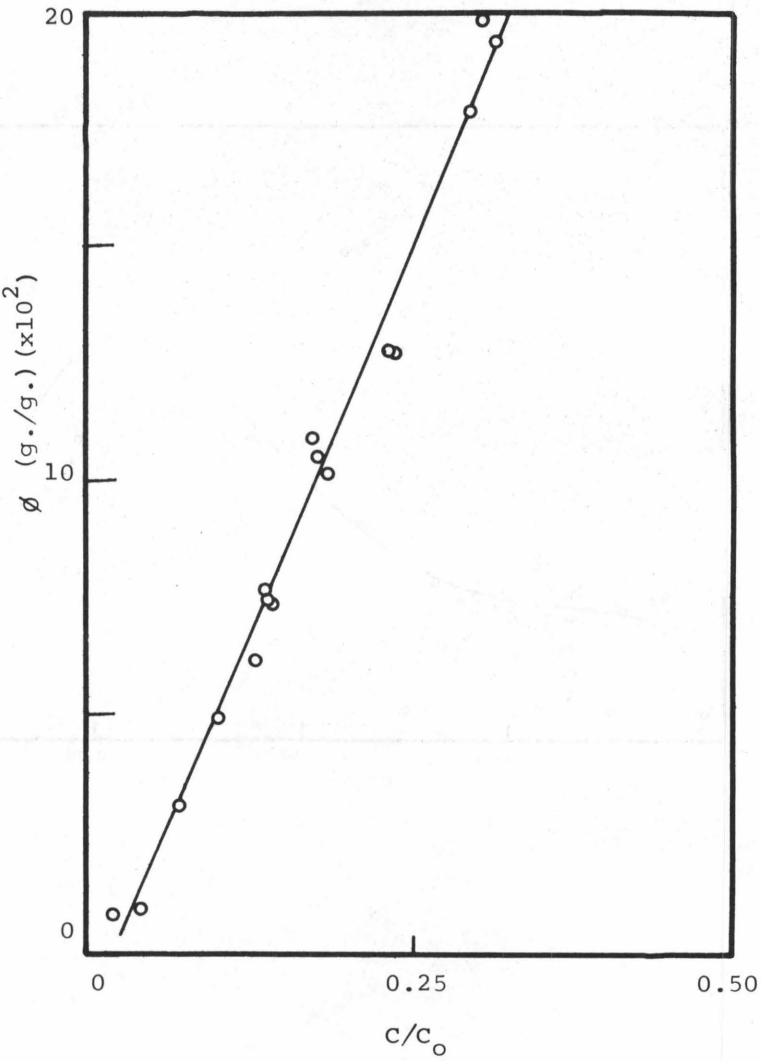


TABLE 10

COMPARISON OF ADSORPTION CAPACITY FOR PHENOL AT A REDUCED CONCENTRATION OF 0.1

Solid	ϕ(gm/gm)	ψ'(gm/m^2)
Aviamide	6×10^{-2}	4×10^{-2}
Graphon	3×10^{-2}	3×10^{-4}
Cab-O-Sil	7×10^{-3}	3×10^{-5}
Alathon	8×10^{-4}	8×10^{-3}
Microthene	6×10^{-4}	2×10^{-3}
Teflon	5×10^{-4}	2×10^{-4}

CONCLUSIONS

The following conclusions were obtained in this study of the adsorption of phenol from aqueous solutions:

1. The surface areas of Cab-O-Sil, Graphon, Aviamide, Alathon, Microthene, and Teflon were 223, 87, 1.5, 0.10, 0.35, and 8.5 m^2/gm, respectively, measured by either low temperature nitrogen or krypton adsorption.

2. The critical surface tensions of Microthene, Alathon, and Teflon were 35, 31.5, and 28 dynes/cm, respectively. The value for Teflon was anomalously high.

3. The contact angles of phenol solutions against Microthene and Alathon were invariably higher for Alathon consistent with the critical surface tensions above.

4. The multiple internal reflection infrared spectrum of Microthene showed more absorption bands than Alathon consistent with the contact angles above.

5. The amount (in grams) of phenol adsorbed on a unit weight basis was 6×10^{-2}, 3×10^{-2}, 7×10^{-3}, 8×10^{-4}, 6×10^{-4}, and 5×10^{-4} on Aviamide, Graphon, Cab-O-Sil, Microthene, Alathon, and Teflon, respectively, at a reduced concentration of 0.1." The results for Teflon are at best marginal due to the extremely small quantity of phenol absorbed.

6. No significant temperature dependence was noted in the adsorption of phenol on carbon.

7. The amount (in grams) of phenol adsorbed on a unit area basis was 4×10^{-2}, 8×10^{-3}, 2×10^{-3}, 3×10^{-4}, and 3×10^{-5} on Aviamide, Alathon, Microthene, Graphon, and Cab-O-Sil, respectively, at a reduced concentration of 0.1.

8. The interaction of phenol with Aviamide appears to involve a sorption process as contrasted to adsorption—a surface phenomenon.

9. The amount of phenol absorbed per unit area by the solid increases as the surface energy of the solid decreases.

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APPENDIX

TABLE 11

ADSORPTION OF PHENOL FROM AQUEOUS SOLUTIONS ON CAB-O-SIL AT 25°C

Run No.	C/C_o	ϕ (gm/gm) ($\times 10^2$)
1	0.01599	0.03937
2	0.01582	0.07382
3	0.03574	0.54258
4	0.03615	0.45087
5	0.05657	0.47423
6	0.05745	0.28741
7	0.12114	0.74280
8	0.12033	0.99042
9	0.18193	0.93821
10	0.18030	1.37127
11	0.21245	1.65658
12	0.21191	1.78405
13	0.25936	2.82990
14	0.26367	1.41466
15	0.44643	3.25939
16	0.44749	2.98796
17	0.54539	4.26919
18	0.55229	2.21323
19	0.66653	2.86116

TABLE 12

ADSORPTION OF PHENOL FROM AQUEOUS SOLUTIONS ON GRAPHON AT 25°C

Run No.	C/C_o	ϕ (gm/gm) ($\times 10^1$)
1	0.00244	0.06176
2	0.00232	0.06261
3	0.00789	0.15141
4	0.00875	0.14643
5	0.02675	0.24961
6	0.02675	0.24961
7	0.06837	0.29178
8	0.07025	0.28222
9	0.13871	0.33583
10	0.13782	0.34228
11	0.13782	0.34228
12	0.16833	0.31909
13	0.16833	0.31909
14	0.22233	0.35386
15	0.22736	0.32295
16	0.29880	0.35701
17	0.29775	0.36400
18	0.38313	0.41797
19	0.37311	0.44569
20	0.46077	0.45257
21	0.46270	0.44319
22	0.59678	0.51371
23	0.60051	0.49035
24	0.67313	0.50088
25	0.67499	0.48932

TABLE 12 (Continued)

Run No.	C/C_o	ϕ (gm/gm) ($\times 10^1$)
26	0.75020	0.69449
27	0.76924	0.59775
28	0.80000	0.74691
29	0.81943	0.63700
30	0.80775	0.70306
31	0.92788	1.64000
32	0.94876	1.51800
33	0.93620	1.57700
34	0.00036	0.08460
35	0.00032	0.08487
36	0.00853	0.17643
37	0.00809	0.17927
38	0.01708	0.22288
39	0.01708	0.22288
40	0.08647	0.30701
41	0.08676	0.30475
42	0.12160	0.31808
43	0.12247	0.31355
44	0.12218	0.31506
45	0.16587	0.33559
46	0.16643	0.33195
47	0.22267	0.35461
48	0.22267	0.35461
49	0.29061	0.40207
50	0.29163	0.39567
51	0.37938	0.40963
52	0.38620	0.37194
53	0.49712	0.50450
54	0.58029	0.54537
55	0.58029	0.54537

TABLE 12 (Continued)

Run No.	C/C_o	ϕ (gm/gm) ($\times 10^1$)
56	0.67239	0.60132
57	0.67239	0.60132
58	0.75797	0.72141
59	0.77847	0.61302
60	0.79925	0.79652
61	0.82457	0.65788
62	0.96825	1.60500
63	0.96825	1.60500
64	0.00158	0.06017
65	0.00012	0.06745
66	0.00378	0.13332
67	0.00421	0.13151
68	0.00404	0.13224
69	0.01472	0.20005
70	0.01493	0.19905
71	0.01578	0.19506
72	0.06796	0.28094
73	0.06812	0.28014
74	0.12630	0.34208
75	0.12815	0.33122
76	0.12969	0.32220
77	0.14650	0.34250
78	0.14771	0.33662
79	0.21307	0.37106
80	0.21364	0.36786
81	0.29653	0.34919
82	0.29332	0.36737
83	0.39469	0.39763
84	0.39369	0.40340
85	0.39269	0.40918

TABLE 12 (Continued)

Run No.	C/C_o	ϕ (gm/gm) ($\times 10^1$)
86	0.46660	0.46415
87	0.47048	0.44577
88	0.58377	0.46057
89	0.57802	0.48905
90	0.66106	0.54060
91	0.66106	0.54060
92	0.74889	0.63981
93	0.74889	0.63981
94	0.77365	0.69214
95	0.78199	0.65690
96	0.93755	1.25500
97	0.94231	1.23500

TABLE 13

ADSORPTION OF PHENOL FROM AQUEOUS SOLUTIONS ON AVIAMIDE AT 25°C

Run No.	C/C_o	ϕ (gm/gm) ($\times 10^2$)
1	0.01233	0.58873
2	0.01223	0.59089
3	0.03713	0.72615
4	0.03713	0.72615
5	0.06316	3.02909
6	0.06507	2.93366
7	0.06547	2.91321
8	0.09360	4.86065
9	0.09468	4.80316
10	0.12399	6.16298
11	0.12513	6.08948
12	0.13673	7.38489
13	0.13754	7.33916
14	0.13293	7.59835
15	0.17084	10.79270
16	0.17084	10.79270
17	0.17463	10.39180
18	0.18274	10.09570
19	0.23511	12.58210
20	0.23242	12.68660
21	0.31530	19.21519
22	0.30563	19.72879
23	0.29810	17.72409
24	0.29918	17.68320

TABLE 14

ADSORPTION OF PHENOL FROM AQUEOUS SOLUTIONS ON MICROTHENE AT 25°C

Run No.	C/C_o	ϕ (gm/gm) ($\times 10^2$)
1	0.00091	0.00103
2	0.00128	0.00090
3	0.06133	0.07236
4	0.11464	0.10837
5	0.11572	0.06019
6	0.17570	0.03367
7	0.17385	0.09261
8	0.21638	0.18788
9	0.21586	0.20355
10	0.33860	0.12940
11	0.43333	0.05929
12	0.43120	0.11853
13	0.42800	0.20732
14	0.56190	0.08911
15	0.56076	0.11877
16	0.63997	0.22600
17	0.76624	0.52488
18	0.75710	0.85596
19	0.83338	1.37439
20	0.01530	0.02850
21	0.01540	0.01900
22	0.01530	0.02610
23	0.01530	0.02850
24	0.03470	0.12220
25	0.03440	0.14260

TABLE 14 (Continued)

Run No.	C/C_o	ϕ (gm/gm) ($\times 10^2$)
26	0.05820	0.15820
27	0.05870	0.11080
28	0.05960	0.01580
29	0.12380	0.19320
30	0.12700	0.02670
31	0.12450	0.15330
32	0.21630	0.01670
33	0.21420	0.15040
34	0.21580	0.05010
35	0.16970	0.49480
36	0.17560	0.22290
37	0.17560	0.22290
38	0.17360	0.31570
39	0.26440	0.35900
40	0.26130	0.50510
41	0.26850	0.15960
42	0.36500	0.21000
43	0.36780	0.07870
44	0.36690	0.11800
45	0.46010	0.06210
46	0.45210	0.42550
47	0.45480	0.31090
48	0.55490	0.10030
49	0.55120	0.03650
50	0.54610	0.21970

TABLE 15

ADSORPTION OF PHENOL FROM AQUEOUS SOLUTIONS ON ALATHON AT 25°C

Run No.	C/C_o	ϕ (gm/gm) ($\times 10^2$)
1	0.00095	0.00008
2	0.00094	0.00058
3	0.00130	0.00025
4	0.00128	0.00099
5	0.00129	0.00091
6	0.06429	0.00436
7	0.11464	0.07825
8	0.17570	0.03012
9	0.17385	0.08285
10	0.21633	0.18464
11	0.21560	0.20602
12	0.33235	0.26276
13	0.43120	0.10923
14	0.42906	0.16379
15	0.56417	0.03234
16	0.56417	0.03234
17	0.56417	0.03234
18	0.86969	0.15651
19	0.85841	0.36364
20	0.01550	0.01640
21	0.01530	0.01830
22	0.03620	0.01590
23	0.03630	0.00790
24	0.05960	0.00670
25	0.05860	0.05330

TABLE 15 (Continued)

Run No.	C/C_o	ϕ (gm/gm) ($\times 10^2$)
26	0.05870	0.04670
27	0.12700	0.01730
28	0.12700	0.01730
29	0.17760	0.09050
30	0.17460	0.18530
31	0.17490	0.17660
32	0.26850	0.12080
33	0.26850	0.12080
34	0.37050	0.12350
35	0.37050	0.12350
36	0.45610	0.19310
37	0.45530	0.22210
38	0.45750	0.14470
39	0.54870	0.11650

TABLE 16

ADSORPTION OF PHENOL FROM AQUEOUS SOLUTIONS ON TEFLON AT 25°C

Run No.	C/C_o	ϕ (gm/gm) ($\times 10^2$)
1	0.00090	0.00071
2	0.00128	0.00045
3	0.00127	0.00056
4	0.00618	0.00025
5	0.06139	0.04513
6	0.11410	0.04029
7	0.11329	0.05129
8	0.17543	0.02070
9	0.21821	0.05570
10	0.21795	0.05898
11	0.33964	0.04978
12	0.42374	0.16026
13	0.56304	0.02887
14	0.63878	0.11746
15	0.76493	0.19304
16	0.77280	0.09680
17	0.87252	0.06614
18	0.01530	0.00570
19	0.01560	0.00230
20	0.01560	0.00170
21	0.01550	0.00340
22	0.03290	0.05390
23	0.03090	0.08300
24	0.03080	0.08520
25	0.03140	0.07620

TABLE 16 (Continued)

Run No.	C/C_o	ϕ (gm/gm) ($\times 10^2$)
26	0.12470	0.04170
27	0.12700	0.00780
28	0.17800	0.03820
29	0.17860	0.02760
30	0.17760	0.04460
31	0.17800	0.03820
32	0.21100	0.07730
33	0.21650	0.00190
34	0.21590	0.00940
35	0.27260	0.01970
36	0.37330	0.00810
37	0.44940	0.15710
38	0.56120	0.12950
39	0.56370	0.09700
40	0.56740	0.04840

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