Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Open-Pore Polyurethane as a Medium for Coal Conversion Process Aqueous Effluent Cleanup

M. S. Denton[a]; S. R. Dinsmore[a]; J. I. Brand[a]; Jack Beams[a]; F. L. Ball[b]
[a] Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee [b] Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

To cite this Article Denton, M. S. , Dinsmore, S. R. , Brand, J. I. , Beams, Jack and Ball, F. L.(1980) 'Open-Pore Polyurethane as a Medium for Coal Conversion Process Aqueous Effluent Cleanup', Separation Science and Technology, 15: 3, 587 — 613

To link to this Article: DOI: 10.1080/01496398008068499

URL: http://dx.doi.org/10.1080/01496398008068499

SEPARATION SCIENCE AND TECHNOLOGY, 15(3), pp. 587-613, 1980

OPEN-PORE POLYURETHANE AS A MEDIUM FOR COAL CONVERSION PROCESS AQUEOUS EFFLUENT CLEANUP

M. S. Denton, S. R. Dinsmore, J. I. Brand, and Jack Beams
Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

and

F. L. Ball
Analytical Chemistry Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

ABSTRACT

A study was made of varying the reaction conditions of in-situ polymerized open-pore polyurethane (OPP). Optimum conditions were determined by electron microscopy and flow-rate studies. Using these conditions, large 1-in. x 12-in. columns were polymerized and compared, by use of a four-column bench-scale adsorption apparatus, with the same type columns filled with three common commercial adsorbents. Breakthrough curves (TOC, total phenol, etc.) of a synthetic and an actual coal conversion wastewater were then plotted for each of these columns.

INTRODUCTION

The first rigid urethane foams were made by O. Bayer in 1947 followed by flexible urethane foams in 1952 by Höchtlen (1). In the last decade, several porous polymers have been used for chromatographic separations. These include polyaromatic polymer beads from styrene with divinylbenzene, porous foam rubber, porous polyethylene, and, finally, elastomeric and thermoplastic foams (2).

The separations medium used in our studies, open-pore polyurethane (OPP), is a unique foam discovered by Jefferson and Salyer (3). OPP is produced by reacting a polyaryl-polyalkylene-polyisocyanate with a polyol in the presence of a catalyst, even at ambient temperatures. The polymer structure is not a network of interconnecting struts left from blown dodecahedral cells, like most foam products, but a very uniform agglomeration of spherical particles with uniform diameters of 1 to 10 μ. Unique among synthetic polymers used in column chromatography, OPP is polymerized in-situ as a highly permeable matrix that strongly adheres to the column walls. This reaction, first carried out in 1968 by Salyer et al. (4) and applied to column chromatography by Ross and Jefferson (5) [subsequently described by Salyer, Jefferson, and Ross (6)], has proven its utility as a GC (5,7) as well as LC (8,9) support.

More recently, OPP has demonstrated a high capacity in collection and preconcentration of phenols (8,10). Similarly, Lynn et al. (9) applied OPP to the separation of substituted anilines and aminophenols by LC. In addition, OPP exhibits a higher efficiency for removal of some polyaromatic hydrocarbons (PAHs) from aqueous solutions than the more expensive, traditional adsorbents (e.g., Amberlite XAD-2 and Bio-Rad AG MP-50), even with micro 5-cm columns (11). Similar columns, 10 cm x 0.4 cm I.D., were used for breakthrough and elution studies of surfactants in wastewater (12). With reasonable removal efficiencies of organics in a broad range of compound classes (e.g., primary amines, phenols, and PAHs), the logical extension of applications of the polymer is to that of aqueous wastes of coal conversion processes. Such breakthrough studies are presented here on a bench scale (as a tertiary cleanup stage) for the removal of amines, nitrogen heterocyclics, phenols, and PAHs — all of which are present in coal conversion wastewater streams.

In addition, studies have been made in our laboratory to control the density, porosity, and surface characteristics (with special attention paid to flow characteristics) of the polymer by varying such reaction conditions as time, temperature, catalyst, and reactant concentrations (i.e., OH/NCO ratio). Scanning electron micrographs have provided us information as to bead size and porosity, as well as new information concerning the nature of the bead surfaces.

METHODS AND MATERIALS

OPP Formulations

As shown in Table 1, an extensive study has been carried out on the effects of varying the reaction conditions on the quality of the polymer. By varying the catalyst used, the OH/NCO functionality ratio, the reaction temperature, the reaction time, and the bulk density, one has an excellent handle on the bead size, porosity, surface characteristics, and selective capacity of the resulting OPP.

Such characteristics were examined by scanning electron microscopy (SEM). For all such studies, an International

TABLE 1

OPP Electron Micrograph Designations and Reaction Conditions

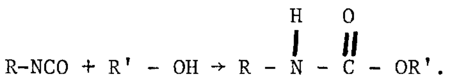
Number	Catalyst	OH/NCO	T(°C)	Time (hr)	Particle size (μ)[a]
OPP-1	EuFOD[a]	2.22	24	59	2.70
OPP-2	DBTDL[c]	2.22	24	59	2.80
OPP-3	None	2.22	24	59	3.30
OPP-4	EuFOD	2.22	0	59	3.30
OPP-5	EuFOD	1.00	0	59	2.90
OPP-6	EuFOD	2.22	-22	59	3.25
OPP-7	EuFOD	2.22	24	24	3.25
OPP-8	EuFOD	2.22	0	24	4.00

[a] Average.
[b] EuFOD = Siever's reagent.
[c] DBTDL = dibutyltindilaurate.

Scientific Instruments (ISI) Super III SEM was used at 15 KV. All samples were coated with a thin layer of a conducting material prior to being analyzed. Five different coatings were used in an attempt to determine the conducting layer that gave the best resolution in the micrographs. Aluminum (Al) and carbon (C) were each deposited by vacuum evaporation while the sample was being rotated; gold (Au) and gold-palladium (Au-Pd) were applied by sputter coating. In the final analysis, the best coating layer was found to be an evaporated C film (a few hundred Å in thickness) followed by a sputtered layer of Au-Pd. This coating technique was used to prepare all but the initial OPP samples reported here.

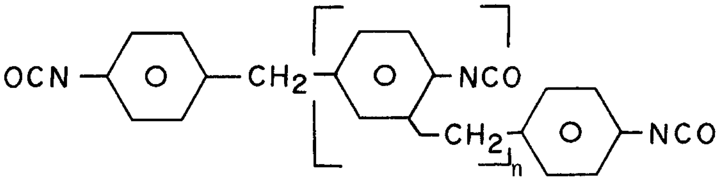
The OPP was prepared simultaneously at the various conditions in analytical-scale (10-cm x 0.4-cm ID standard laboratory glass) and bench-scale (1-in. x 12-in. Pyrex glass pipe) columns, as well as polyethylene tubes for later analysis by electron microscopy (EM). All columns were thoroughly cleaned by filling them with a 50% NaOH solution for at least 4 hr. Even though OPP will adhere quite well to glass, the inside of each column was etched with 48% HF overnight, which greatly strengthens the OPP-to-wall bond. Such a procedure leaves even the Pyrex tempered glass with a milky, textured appearance. Solid Teflon plugs were used to seal the bottoms of columns during the NaOH and HF steps. No column-end frits were necessary once polymerization was complete.

The actual synthesis of OPP is accomplished by step-growth polymerization of polyisocyanates and polyols. The addition of a hydroxy group to an isocyanate yields a substituted amide ester of carbonic acid, i.e., polyurethane, and is shown in the following reaction:

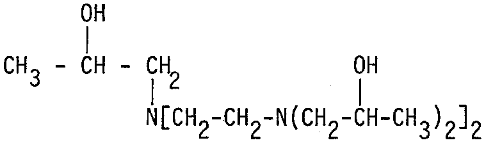


$$R\text{-}NCO + R' - OH \rightarrow R - \overset{\overset{\displaystyle H}{|}}{N} - \overset{\overset{\displaystyle O}{\|}}{C} - OR'. \qquad (1)$$

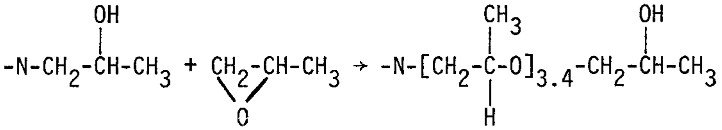
Mondur MR from Mobay Chemical Coproration (Pittsburgh, PA) (4,4'-diphenylmethane-diisocyanate, with lesser amounts of tri-, tetra-, and pentaisocyanates; average of 2.7 NCO groups/molecule and equivalent weight of 132) is the source of isocyanate used:


(2)

Union Carbide Corporation (Charleston, W.VA) supplies the polyol, NIAX Polyol LA-475 (polypropylene glycol), which is a pentahydroxy compound formed by total oxypropylation of diethylene triamine to the intermediate:


$$\mathrm{CH_3-\overset{OH}{\overset{|}{C}H}-\underset{\displaystyle N[CH_2\text{-}CH_2\text{-}N(CH_2\text{-}\overset{OH}{\overset{|}{C}H}\text{-}CH_3)_2]_2}{\underset{|}{CH_2}}}$$
(3)

Oxypropylation continues at the hdyroxyl hydrogens until an equivalent weight of 118 is reached (5-OH groups/molecule).


$$\mathrm{-N-CH_2-\overset{OH}{\overset{|}{C}H}-CH_3 + \underset{O}{\underbrace{CH_2-CH}}-CH_3 \rightarrow -N-[CH_2-\overset{CH_3}{\underset{H}{\overset{|}{\underset{|}{C}}}}-O]_{3.4}-CH_2-\overset{OH}{\overset{|}{C}H}-CH_3}$$
(4)

The mechanism for the formation of OPP has been explained in detail by Ross (2) and is given here briefly as follows. The isocyanate reacts with the active hydrogen of the polyol to form liquid-soluble, short-chain polymers. These increase in length and MW until they are no longer soluble. After this gel formation, the chain ends undergo further reaction until in-situ precipitation takes place.

All OPP formulations used in this study were of a bulk density of 0.197 g/ml and a OH/NCO functionality ratio of either 1.00 or

2.22. Just prior to polymerization, the reactants were weighed and dissolved in a 60/40 vol % toluene/carbon tetrachloride solution (of a similar density, 1.17 g/ml, to the OPP to avoid settling) (7). The catalyst used, 1 mg per total ml of solution, was added to the polyol, toluene/carbon tetrachloride mixture prior to polymerization. Catalysts are extremely important in achieving foams with suitable characteristics. The tertiary amine back bone in LA-475 can act as a self-contained catalyst for the polymer reaction. However, tin catalysts, for example, have the advantage of promoting the isocyanate-hydroxyl reaction rather than the isocyanate-water reaction. Some common organo-metallic catalysts are: dibutyltindioctoate, stannousoleate, stannousoctoate, and dibutyltindilaurate (DBTDL). The choice of these and the amount employed affect the open or closed cell properties of the foam (1) (See Table 1 and Figs. 3 and 4). The two catalysts used here were DBTDL from Cincinnati Milacron (Cincinnati, OH) and the lanthanide shift reagent, Siever's Reagent [Resolve - Al EuFOD^{TM}, 2,2,-dimethyl-6, 6, 7, 7, 8, 8, 8-heptafluoro-3, 5-octanedione, europium(III) derivative, or $Eu(fod)_3$] now available from Aldrich Chemical Company. Similar to those reported by Sievers et al. (10,11), weights of the individual components are given as follows:

	OH/NCO = 1.0	OH/NCO = 2.22
LA-475	2.84 g	4.00 g
Mondur MR	3.16 g	2.00 g
60/40 Toluene/C Cl_4	25 ml	25 ml
Catalyst	31.8 mg	32.3 mg

Polyol and catalyst (in solvent) were mixed thoroughly with the isocyanate (also in solvent) and poured into columns. Teflon^{TM} plugs sealed the column ends during polymerization, while the tops were left open to allow escape of any gases formed (to avoid column voids). The columns were then placed in locations at their appropriate temperature (Room T = 24°C, refrigerator T = 0°C, and freezer T = -22°C, see Table 1). After appropriate reaction times, 24 to 60 hr (see Table 1) the columns were thoroughly and consecutively flushed with n-heptane, methanol, and distilled water (DW). It was found that flushing with n-heptane again and allowing to dry and store in air increased the life of the column.

Bench-Scale Adsorption Columns and Apparatus

In addition to the bench-scale OPP-8 columns prepared as previously mentioned, three identical columns of common adsorbents were slurry-packed in DW. Prior to packing, all adsorbents were passed through sieves and appropriately sized. These mesh values and the OPP-8 reaction conditions are given in Table 2. Also

TABLE 2

Bench-Scale Adsorption Columns[a]

Type	Reaction conditions[b]	Mesh[c]	Surface area (m^2/g)[d]	Flow rate (ml/hr)[e]
OPP	EuFOD/2.22/0/24		0.9	204
Columbia (Petroleum based activated charcoal, Union Carbide)		30-50	1000	276
Ambersorb XE-348 (Carbonaceous adsorbent, Rohm and Haas)		20-50	500	1278
XAD-2 (Rohm and Haas)		20-50	330	3738

[a] 1-in. x 12-in. glass pipe.

[b] Catalyst/OH-NCO functionality ratio/reaction temperature,/°C reaction time.

[c] U.S. Sieve series.

[d] N_2,

[e] Gravity flow rate with 68.5 cm of head pressure. Value is the average of the two trials.

reported in this table are the surface areas obtained by Brunauer, Emmet, and Teller (BET) N_2 surface area measurements, and the gravity flow rates obtained with 68.5 cm of water head pressure. Since the surface area for the OPP came out so low (0.8 m^2/g) by the normal N_2 BET method, it was rerun on a high-pressure N_2 BET system. Essentially the same value was obtained (0.9 m^2/g). Figure 1 shows the bench-scale adsorption apparatus into which these columns are placed. The four columns used in this study (from left to right in Fig. 1) are as follows: OPP-8 as explained in Table 1, Columbia ACC activated charcoal (coke base) from Union Carbide Corporation, and Ambersorb XE-348 carbonaceous adsorbent (spherical resin) and XAD-2 — both from Rohm and Haas (Philadelphia, PA).

Feed Solutions

Having done extensive work in the past on characterization and identification of components in coal conversion wastewaters, the general classes of compounds present were known. With this in mind, a synthetic feed was made up with representative compounds from a number of these classes including the following: aniline (primary amine), 2, 4, 6-trimethylpyridine (simple nitrogen-ring compound), 2,6-dimethylquinoline (nitrogen heterocyclic), phenol (parent of phenolic class), 3,4-xylenol (dimethyl phenol), and indole (nitrogen heterocyclic). The synthetic feed was made up to 10ℓ in DW in such a manner as to give 100 ppm of each component.

The actual coal-conversion wastewater used as a feed in these studies was the scrubber water from an ORNL Bench-Scale Coal Carbonizer (BSCC). The carbonizer run was made with Wyodak subbituminous coal from Gillette, Wyoming and CO_2 as the fluidizing gas. The BSCC was operated at about 1100 to 1300°F and 2 psig with a short coal residence time. The resulting aqueous scrubber was air stripped (see stripper, left side of Fig. 1) at room temperature until the total organic carbon (TOC) level was stabilized at 430 ppm (reduced from 890 ppm). This effluent (1.2 ℓ, pH 7.5) was then

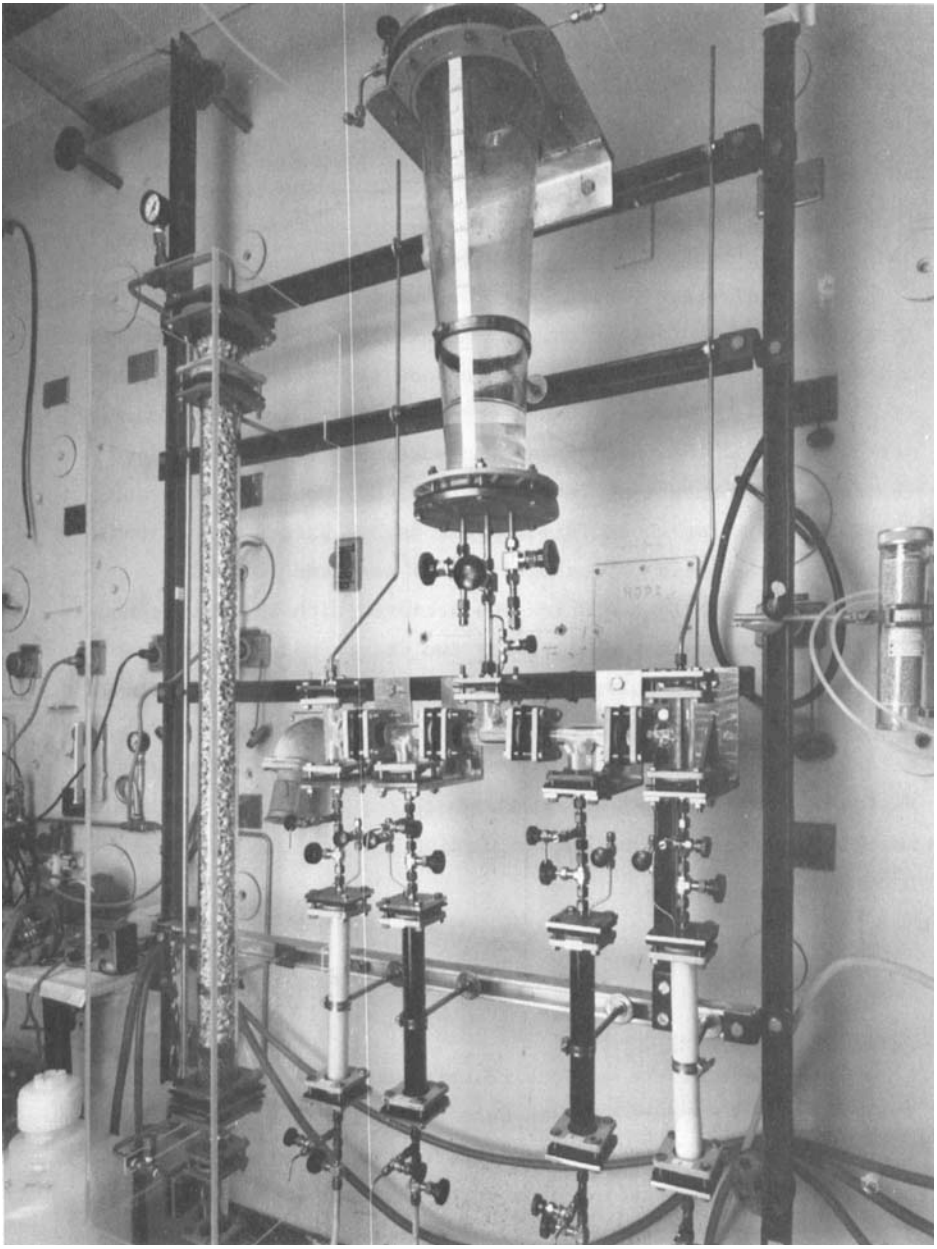


FIGURE 1. Bench-scale adsorption apparatus. Columns are (from left to right) OPP, Columbia, Ambersorb XE-348 and XAD-2.

ozonated in the batch mode for 30 min, at ambient temperature, and 272 ml/min flow of O_2/O_3 mixture (7.5 mole % O_3). This solution was subsequently diluted (1175 ml to 4000 ml in DW), resulting in a feed with the following characteristics: pH = 5.8, TOC = 172 ppm, and total phenol (TP) = 36 ppm. For flow rates of this feed and the synthetic feed, see the individual figures.

Analytical Methods and Instrumentation

All total organic carbons (TOCs) were done on a Beckman Instruments, Inc. (Fullerton, CA) Model 915-B Total Organic Carbon Analyzer by subtracting inorganic carbon (IC) from total carbon (TC) readings. The 4-aminoantipyrene (4-AAP), direct photometric method was used for total phenol measurements (13). A Gilford Instrument Laboratories, Inc. (Oberlin, OH) Model 250 was used to monitor 510 nm for these TP measurements. A Waters Associates (Milford, MA) liquid chromatograph (LC) was used for all separations. Gradient elution was achieved with the Waters Model 660 solvent programmer controlling two Waters Model 6000A pumps. A syringe injection valve (Rheodyne Inc., Model 7105, Berkeley, CA) was used for all sample introduction onto a 30-cm x 0.46-cm Waters μ-Bondbak C-18 column. Detection was accomplished with a Waters 440 Dual-Channel Absorbance Detector monitoring 254 and 280 nm. Integration and dual-pen recording was done with a Waters Data Module.

RESULTS AND DISCUSSION

Electron Microscopy

The effect of the various reaction conditions summarized in Table 1 on the product OPP can only be seen by the use of scanning electron microscopy (SEM). Our interest in SEM studies of OPP began with the publication of several EMs done by Ross (2) and Sievers (8,10). These OPP electron micrographs exhibited beads with a great deal of fine surface structure (brain-like in appearance). The EMs reported were done on a Cambridge Stereoscan

Mark II by coating the OPP with a 100 to 200 Å layer of Al by thermal evaporation in vacuo. The question arose as to whether this fine structure was due to the coating or scanning technique, or purely to polymerization conditions (14). Our preliminary coating attempts with sputtered gold (Au) showed poor resolution, but no evidence of such structure. This led us to a brief study of the effect of coating techniques, which is outlined in Fig. 2. (All EMs of Figs. 2 and 3 are of OPP-1). If the surface structure was purely from coating techniques, the left column (OPP-1, Al) should have been very similar to those reported by Ross and Sievers; however, the beads are quite smooth. Also using vacuum evaporation (like Al), is the carbon (C) technique shown in the middle column (OPP-1, C). This method gives better resolution, but no fine structure. Finally, Au-Pd was sputter coated onto OPP-1 with only a slight trace of surface deformations (Fig. 2, OPP-1, Au-Pd). As mentioned previously, the best coating technique was that obtained by an evaporated C film followed by a sputtered layer of Au-Pd. The efficacy of this combined technique is clearly demonstrated in Fig. 3. It was concluded that the fine structure sometimes present in OPP is, in fact, a product of polymerization conditions. (Figs. 4 through 7 are all EMs of OPP coated with C/Au-Pd.)

OPP-1, shown in Fig. 3, was produced using the same catalyst as Sievers (Siever's Reagent). Varying or eliminating this catalyst has profound consequences on the resulting OPP, as can be seen on the left or right-hand side of Fig. 4, respectively. OPP-2, using dibutyltindilaurate (DBTDL) as a catalyst, demonstrates incompletely formed spheres. No catalyst added as in OPP-3 exhibits the least formation of spheres, the most general roughness, and, oddly enough, the most surface fine structure found in our studies. Again, it should be noted that the tertiary backbone present in the polyol can serve as a self-contained catalyst (7). The effect of reaction temperature (Fig. 5) plays an important role in porosity, and, therefore, flow rates which are quite important in cleanup processes. Both OPP-4 and OPP-6 are identical to OPP-1 (Fig. 3), with the

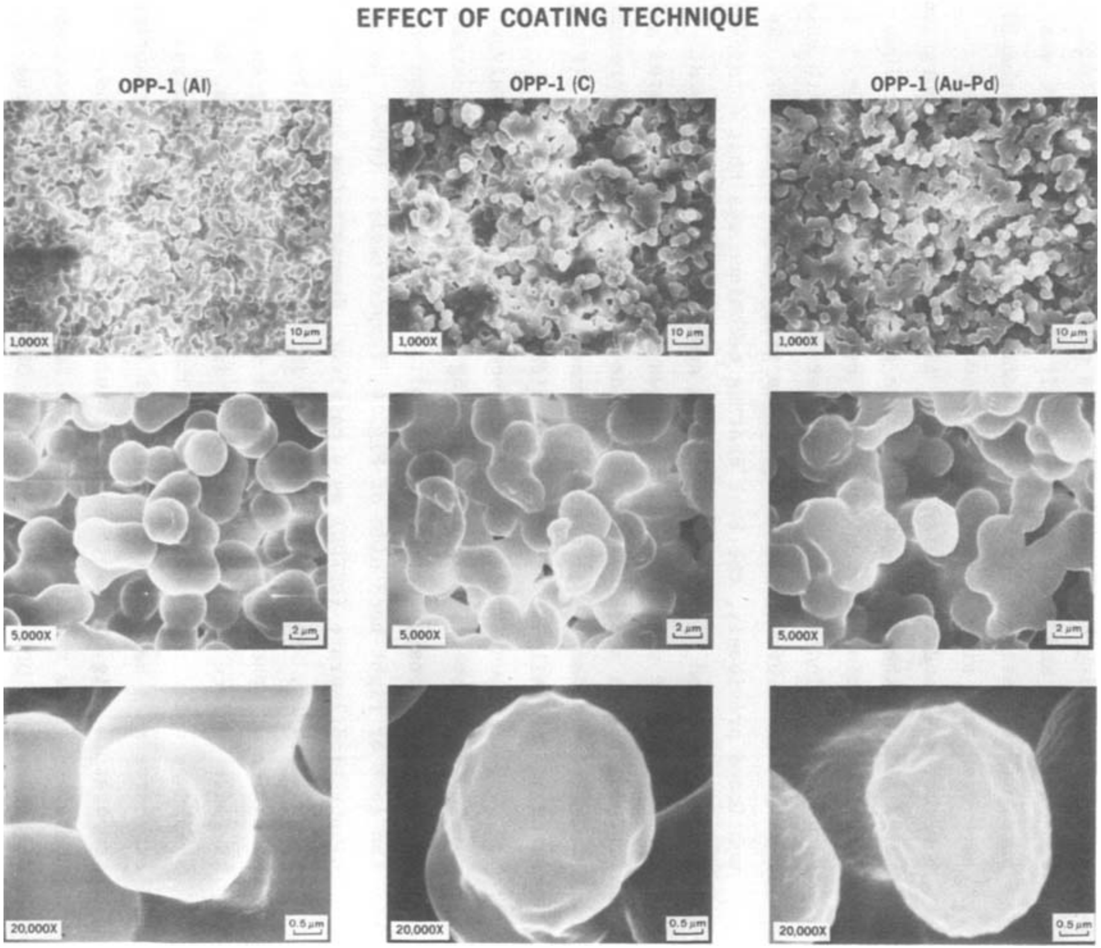


FIGURE 2. Effect of coating technique.

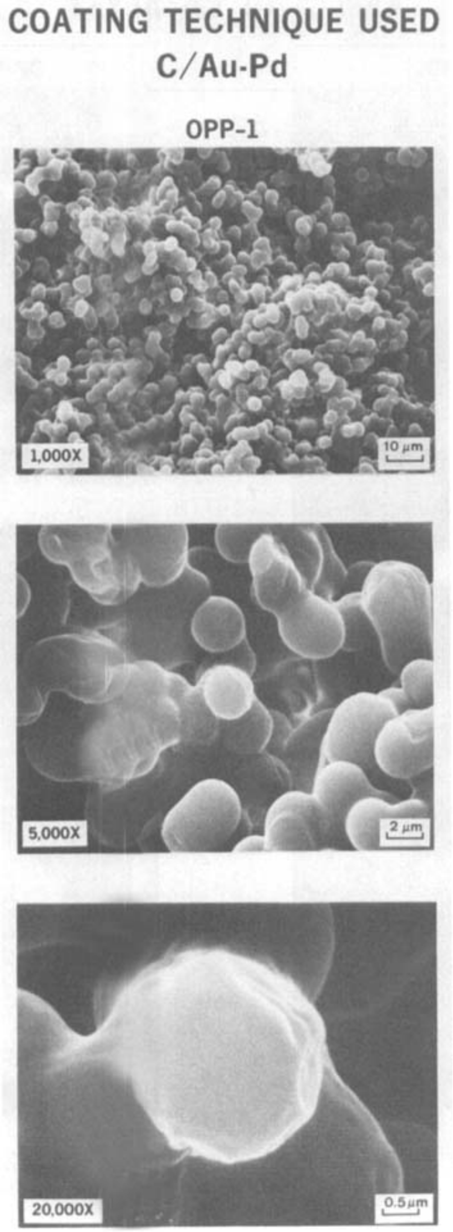


FIGURE 3. Coating technique used.

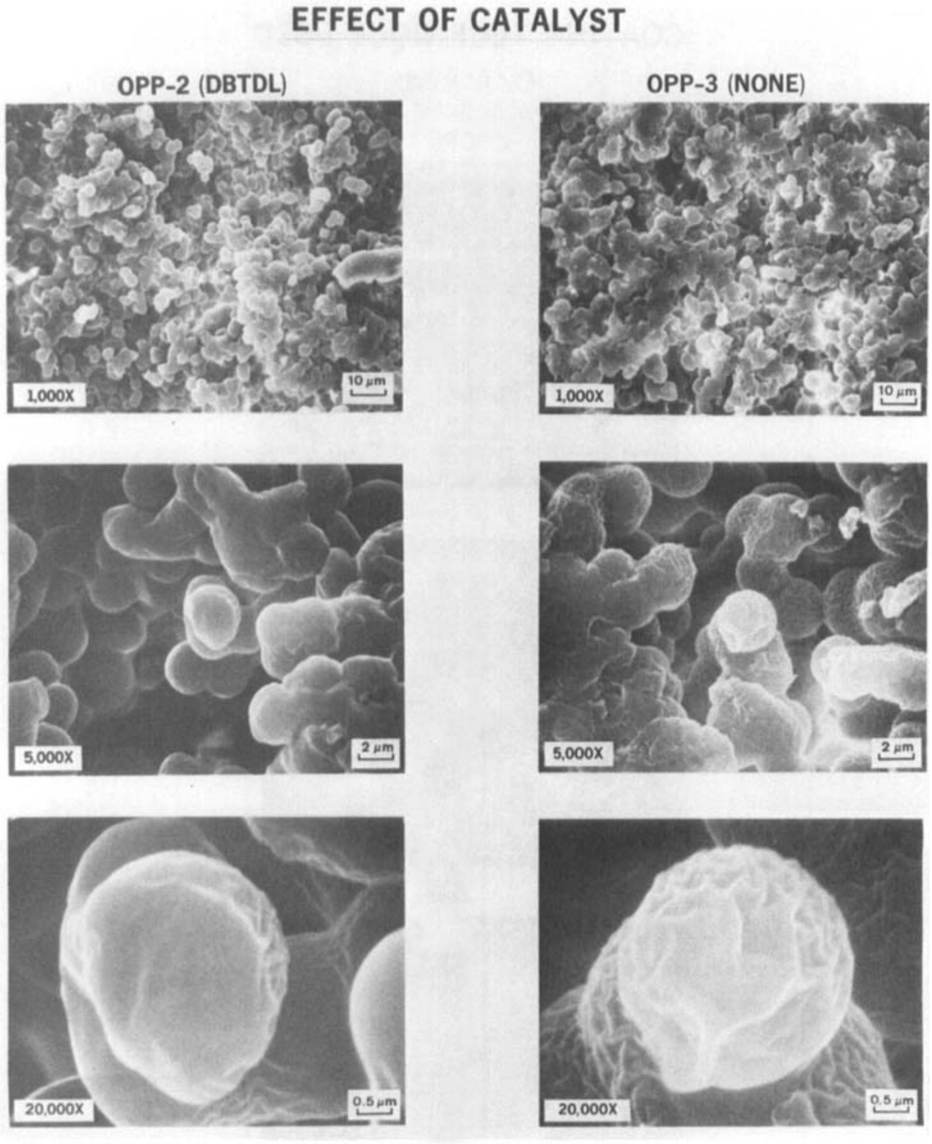


FIGURE 4. Effect of catalyst.

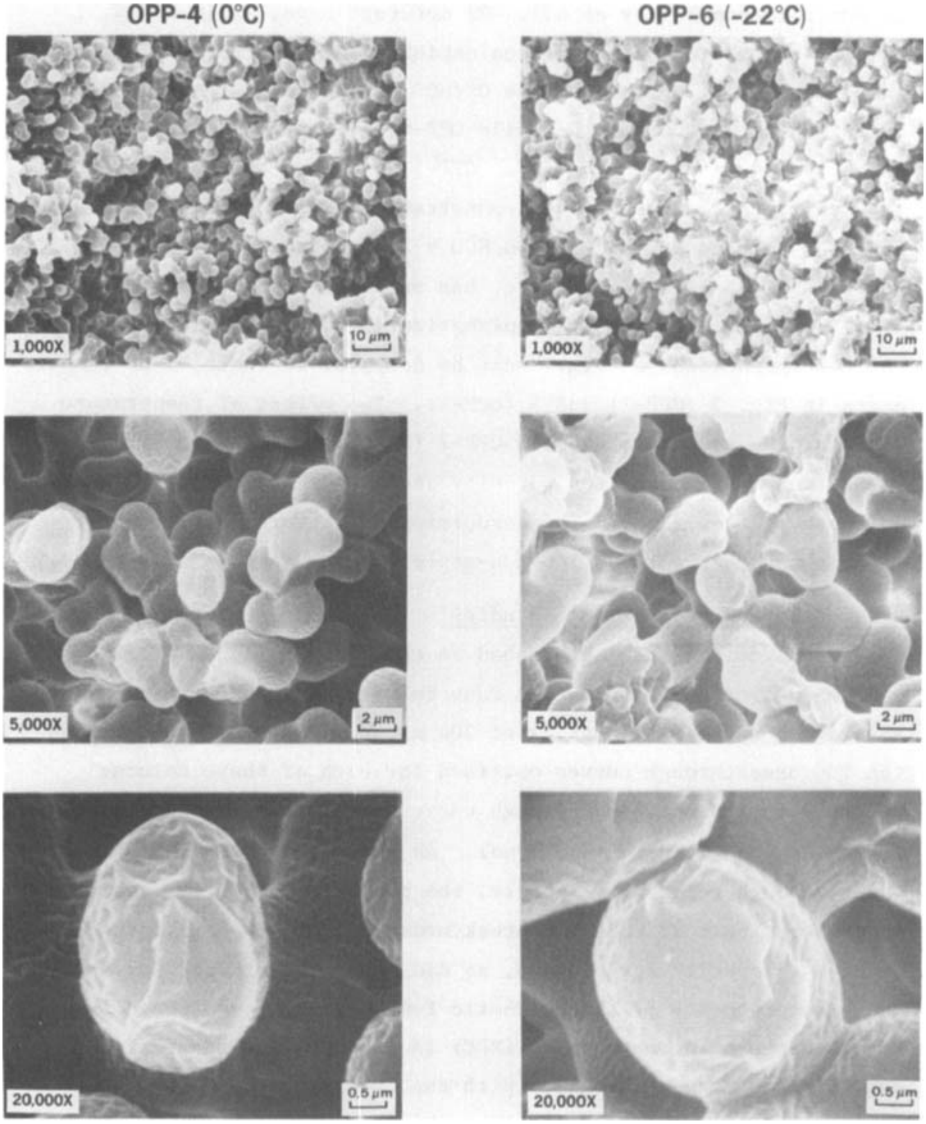


FIGURE 5. Effect of temperature.

exception of temperature. As one decreases the reaction temperature, the spheres become more oblong and misshapen, and at a point (-22°C) do not form completely at all. Of interest here, as in OPP-3, the low-temperature formulations exhibit fine structure. Figure 6 shows the effect of varying the OH/NCO functionality ratio. Here, OPP-5 has an OH/NCO of 1.0, while OPP-4 is identical with the exception of an OH/NCO of 2.22. OPP-5 is one of the most uniform and well-formed polymers but demonstrates a lower capacity for organics such as pyrene than OH/NCO = 2.22 polymers (10 and 11). Reaction time, like temperature, has an effect on polymer porosity since, without flushing, the polymerization would continue for days. The 24-hr reactions of Fig. 7 can be compared to their 59-hr counterparts in Fig. 3 (OPP-1) and 5 (OPP-4). The effect of temperature can again be seen here between OPP-7 (24°C) and OPP-8 (0°C). The latter exhibits better porosity and larger spheres, both leading to improved flow rates. These superior characteristics of OPP-8 made it the choice for all bench-scale columns used in this study.

Synthetic Feed Breakthrough Studies

The synthetic feed described in the Methods and Materials section was passed through the four columns of the bench-scale adsorption apparatus (Fig. 1) at 204 ml/hr. Figure 8 demonstrates the TOC breakthrough curves obtained for each of these columns. Figure 9 is another breakthrough curve of this same run except that it monitors only the total phenol. As shown in Fig. 8 where XAD-2 broke through relatively rapidly, the phenols apparently made up a significant part of this TOC breakthrough. The OPP-8 exhibited excellent capacity for phenols, as did the Ambersorb and Columbia. The six components of the synthetic feed are shown separated by reversed-phase chromatography (RPC) in Fig. 10 (see figure for chromatographic conditions). With the excellent resolution and reproducibility of retention times obtained, it was possible to run a series of standards and digitally integrate each of the peak areas. Thus quantifying each component in the mixture (C values), relating these values to the initial feed concentration (C_o), and plotting C/C_o versus

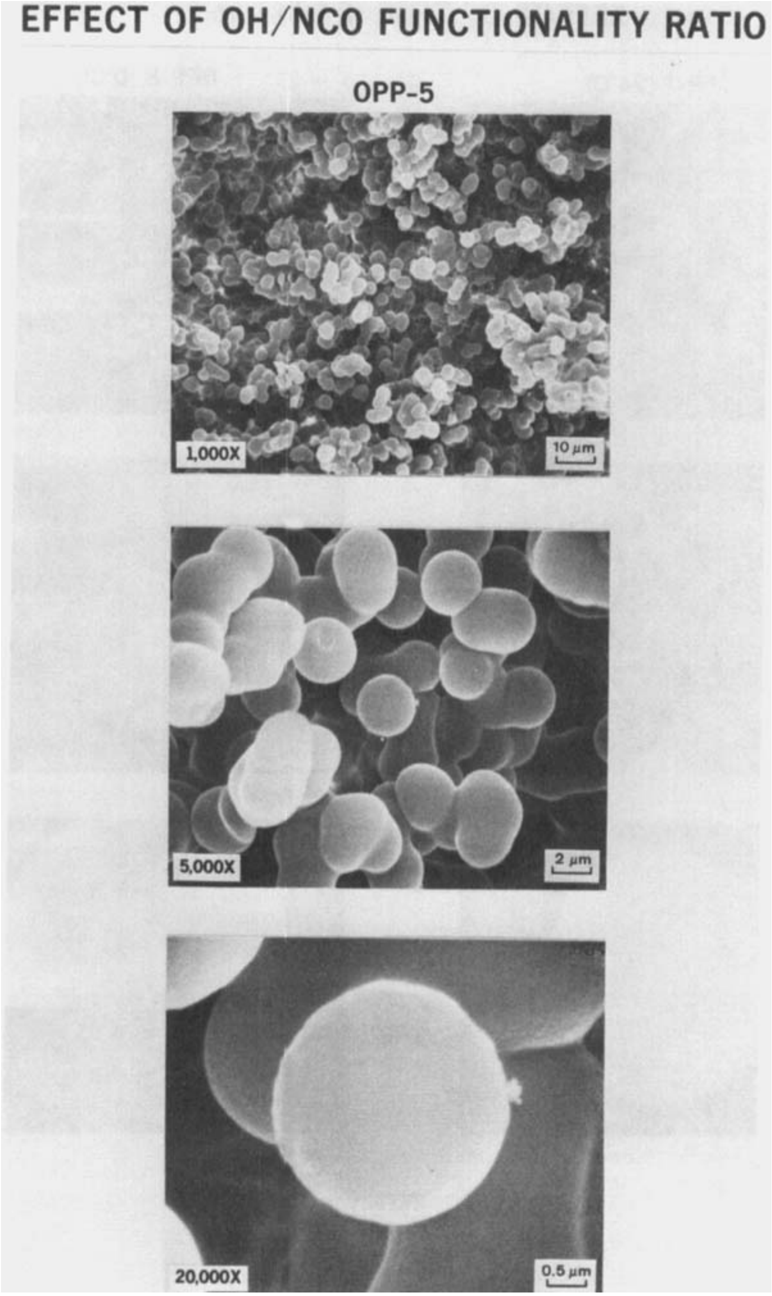


FIGURE 6. Effect of OH/NCO functionality ratio.

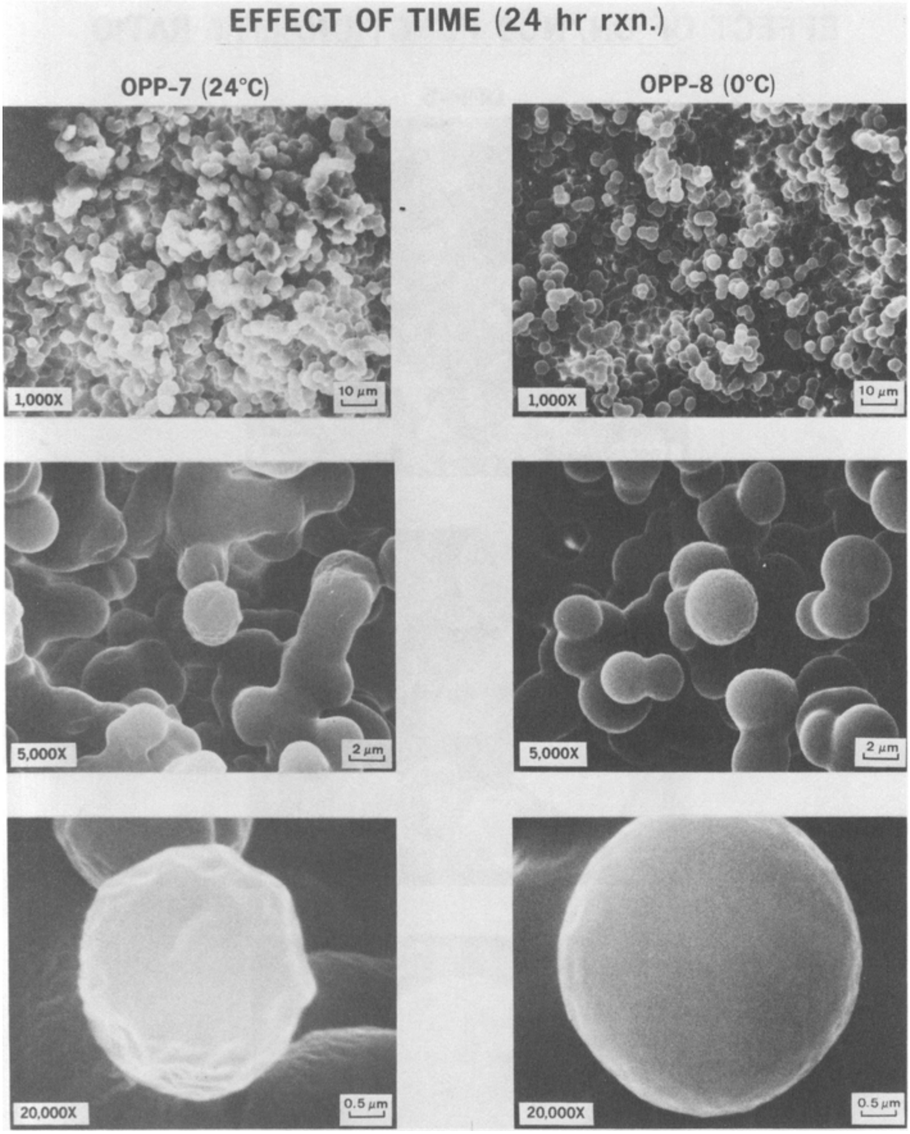


FIGURE 7. Effect of time.

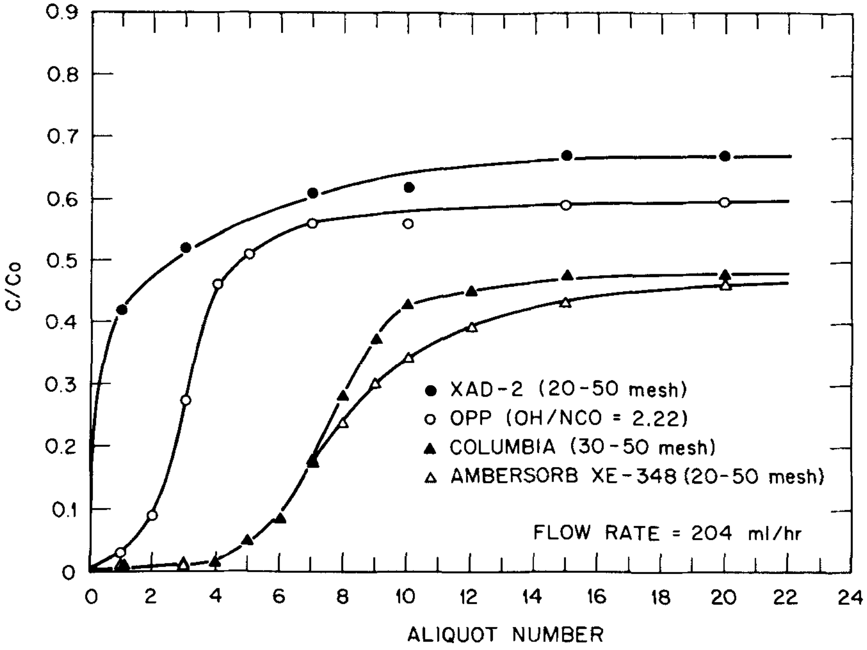


FIGURE 8. TOC breakthrough curves for synthetic feed on 1-in. x 12-in. columns of the bench-scale adsorption apparatus. C/C_0 = concentration (i.e., TOC in ppm) of effluent divided by concentration of feed. One aliquot = 34 ml (i.e., 10 min at 3.4 ml/min).

the calculated number of milligrams of each material eluted at each aliquot collected during the experiment allows one to look at the individual breakthrough curves. Figure 11 illustrates plots for XAD-2 (A) and OPP-8 (B), for example, ultimately making up the TOC breakthrough curves shown in Fig. 8. It is apparently the primary amine and the pyridine that break through for both the XAD and the OPP. Phenol also breaks through, but only to a slight degree with OPP-8 (as shown in Figs. 9 and 11B). With such individual compound class breakthrough information, one can more readily design a tertiary cleanup

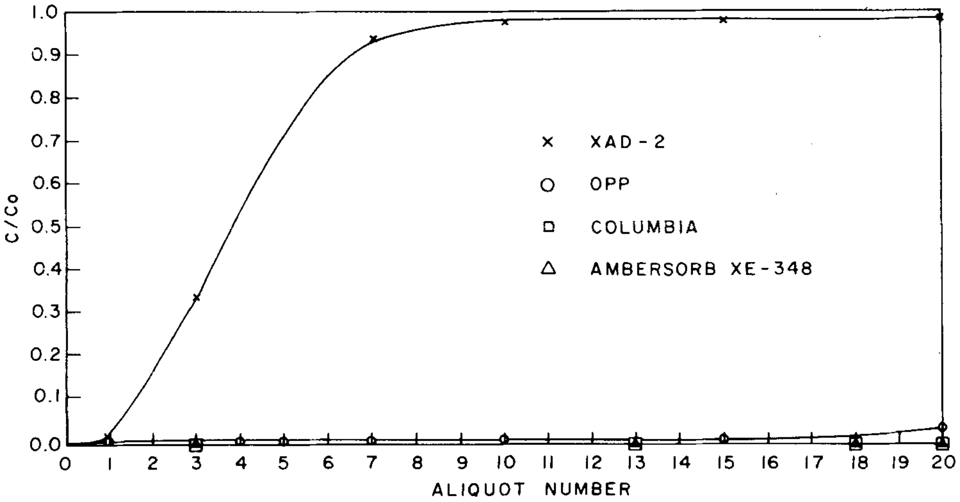


FIGURE 9. Total phenol (i.e., phenol and 3,4-xylenol) breakthrough curves for synthetic feed on 1-in. x 12-in. columns of the bench-scale adsorption apparatus. Total phenol by the 4-AAP method (absorbance at 510 nm). C/C_0 = total phenol in effluent divided by total phenol in the feed, where C_0 = 111.8 ppm total phenol. One aliquot = 34 ml.

process to suit one's particular need. The actual TOC breakthrough data and characteristics for each of the four sorbents is shown in Table 3, where the capacities are calculated at $C/C_0 = 0.3$. When figured on a capacity per weight of sorbent basis, OPP ranks nearly as well as activated charcoal. This low density of the polymer would be quite important in a large process design.

OPP has been demonstrated to be intermediate in capacity for these compounds between the XAD resin and the carbon adsorbents (Fig. 8) and exhibits very little breakthrough of phenols (Figs. 9 and 11B). The in-situ polymer also has one further advantage in that it is more readily eluted with organic solvents than the other sorbents. Figure 12 illustrates the elution characteristics for XAD-2 and OPP-8 using anhydrous methanol. With the same amount of methanol,

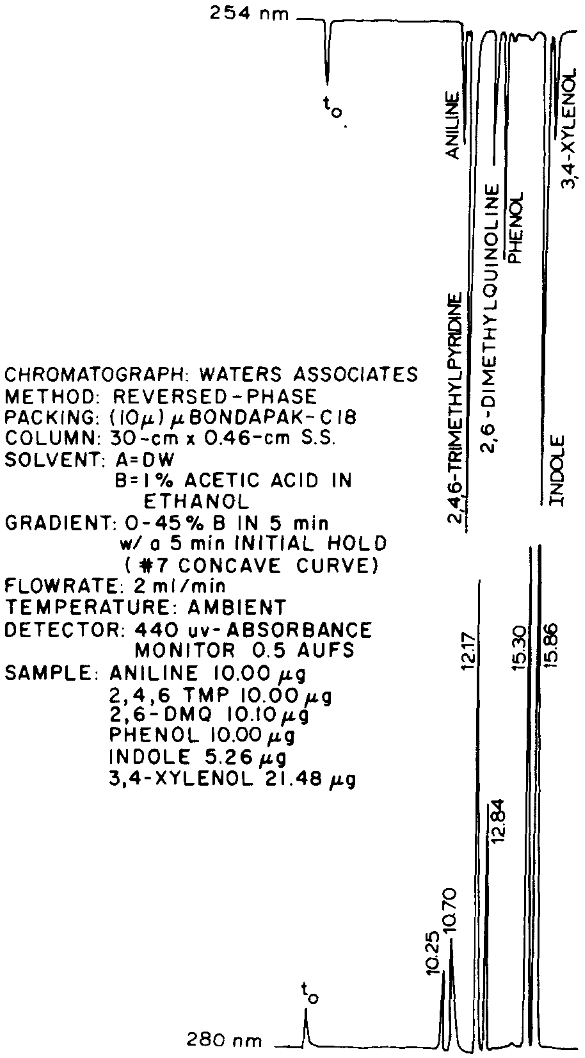


FIGURE 10. Reversed-phase chromatogram of the six-component synthetic feed used for breakthrough studies on the bench-scale adsorption apparatus.

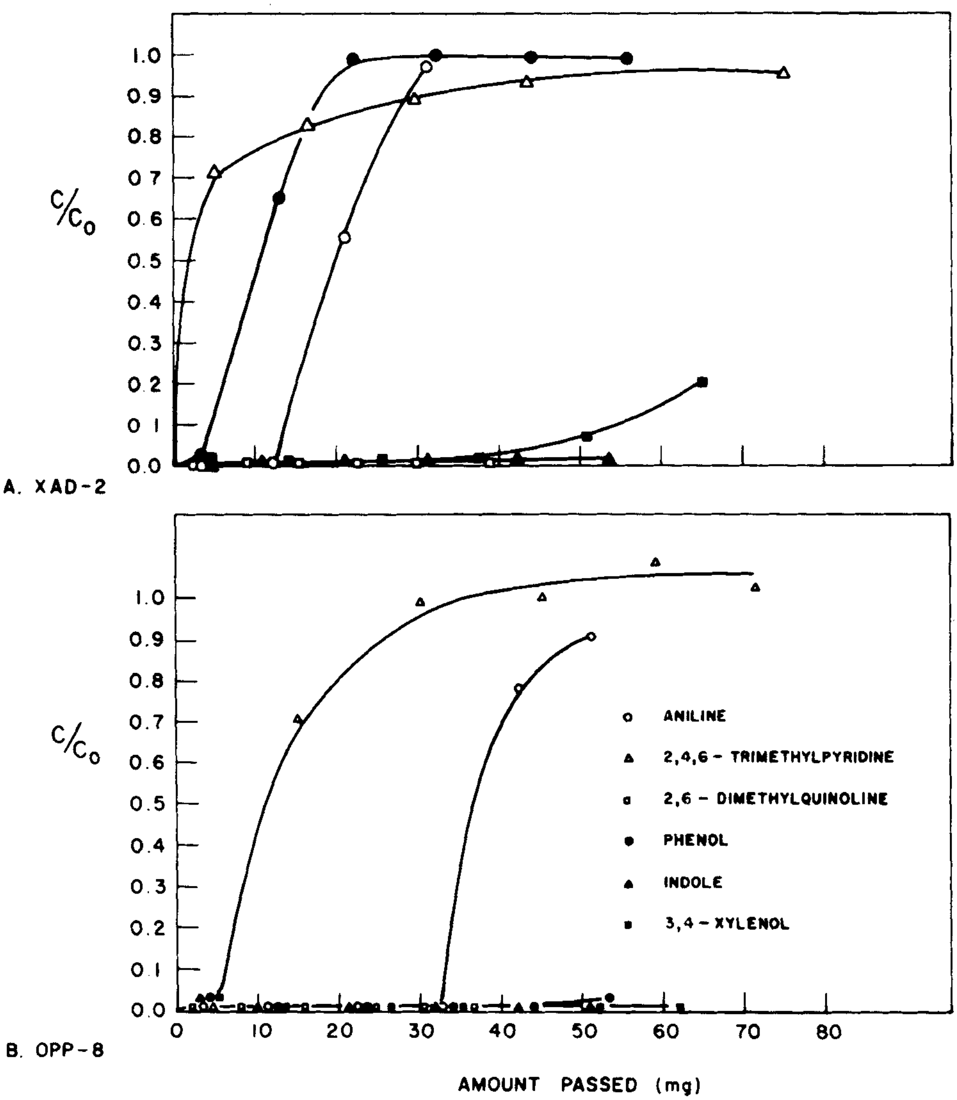


FIGURE 11. Breakthrough curves for the six individual components of the synthetic feed.

TABLE 3

TOC Breakthrough Capacities for Four Sorbents for a Synthetic Wastewater

Type	Sorbent Characteristics			Capacities at $C/C_o = 0.3$[c]	
	Weight[a] (g)	Volume[a] (ml)	Density[b] (g/ml)	TOC (mg)	TOC/g Sorbent (mg/g)
OPP	26.0	155	0.17	94.2	3.6
Columbia activated charcoal	65.5	150	0.44	257.8	3.9
Ambersorb XE-34%	90.4	135	0.67	281.3	3.1
XAD-2	48.5	135	0.36	31.1	0.64

[a] Measured quantity.

[b] Calculated from measured values.

[c] Breakthrough curves were plotted from measured TOC values (see Fig. 8). Numerical integration (by computer) of the area between these curves and $C/C_0 = 1.0$ from the beginning of the run until the curves reach $C/C_o = 0.3$ (defined here as the breakthrough point) gave the total TOC capacities.

the Ambersorb XE-348 and the Columbia ACC exhibited negligible TOC elution. This could be a very important point in resource recovery or in minimizing solid, hazardous disposal problems.

Carbonizer Aqueous Scrubber Breakthrough Studies

As in Fig. 8, Fig. 13 illustrates TOC breakthrough curves for the four adsorbents. In this case, aqueous scrubber waste from a coal carbonizer with a pH of 5.8, TP of 36 ppm, and TOC of 172 ppm was passed through the system at 240 ml/hr. The Ambersorb XE-348 and Columbia ACC again exhibited excellent TOC capacities. Somewhat of a reversal has occurred with the XAD-2 and OPP-8, possibly due to a much lower phenol content in this particular waste (the TOC is also approximately one-third of that of the synthetic feed).

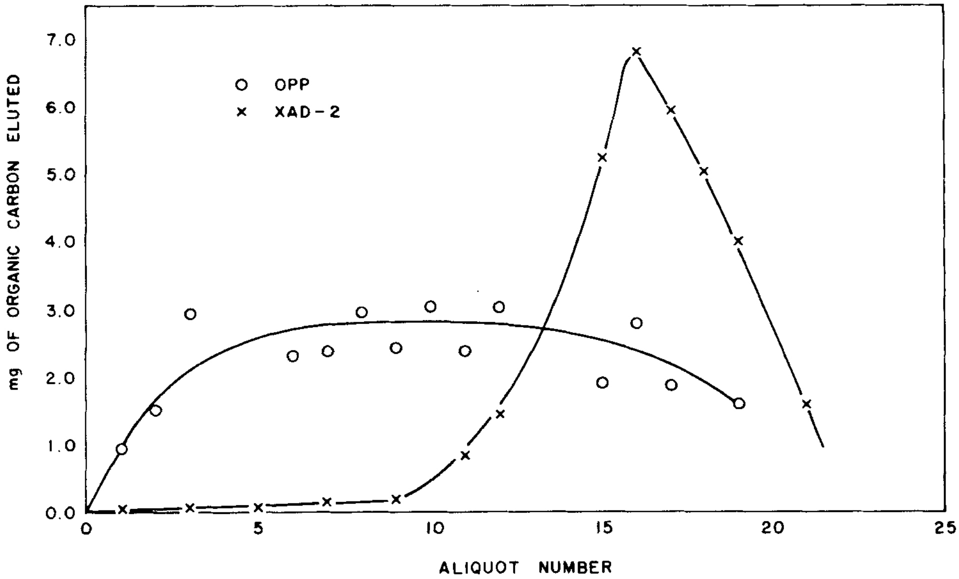


FIGURE 12. Methanol elution curves for the synthetic feed adsorption experiment (2-ml aliquots).

It should be noted that with the number of aliquots taken, C/C_o values never go over about 0.5. Also, the OPP curve for this coal carbonizer aqueous waste (Fig. 13) is nearly identical to its corresponding curve for the synthetic feed (Fig. 8).

In summary, in-situ foamed open-pore polyurethane offers a very promising alternative to commonly used resins and charcoals for wastewater cleanup. Comparative cost and elution characteristics (it can even be completely dissolved in certain acids for total recoveries) are among its advantages. The primary disadvantage of OPP is that it will, after very large volumes of water, finally break away from the glass walls. A solution to this problem is being investigated by varying column treatment and design.

Future Developments

Additional work is now being carried out on an analytical scale (10-cm x 0.4-cm ID columns). With such columns, a greater variety

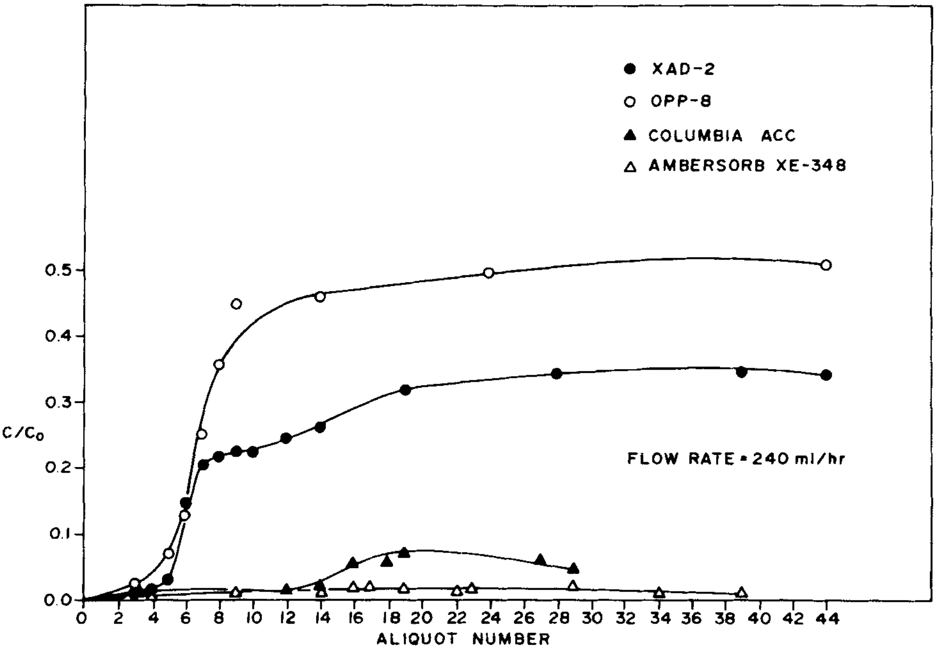


FIGURE 13. TOC breakthrough curves for an aqueous scrubber waste from a bench-scale coal carbonizer run. The bench-scale adsorption apparatus was used with 4 ml/min flow rates.

of adsorption media (including various formulations of OPP) can be conveniently investigated. Effluents from these columns during breakthrough studies can be easily collected and, after extracting them into a suitable organic solvent (e.g., methylene chloride), run on glass capillary gas chromatography. This allows the investigation of the breakthrough behavior of the individual components of very complex solutions (e.g., o-, m-, and p-cresol and 3,4-,2,3-,3,5-,2,4-, and 2,6-xylenol), thus providing valuable information concerning which compounds in aqueous wastes are removed, degraded, or refractory to various cleanup processes. Scale-up studies are underway relating analytical-to-bench-scale operations. Additional coal conversion wastewater streams are also being examined.

ACKNOWLEDGMENT

This research was sponsored by the Office of Health and Environmental Research, U.S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation. Union Carbide Corporation and the United States Government expressly reserve the right to print, reprint, publish, copy, vend, translate, and use any or all material contained herein.

REFERENCES

1. David and Stanley, Analytical Chemistry of the Polyurethanes, Part 3, Vol. XVI, Wiley-Interscience, New York, 1969.

2. W. D. Ross, "Open-Pore Polyurethane - A New Separation Medium," Chapter in Separation and Purification Methods, Vol. III, No. 1 (E. S. Perry, ed.), Marcel Dekker, Inc., New York, 1974.

3. R. T. Jefferson and I. O. Salyer, U.S. Patent 3,574,150, April 6, 1971.

4. I. O. Salyer, J. L. Schwendeman, and R. T. Jefferson, "Polyurethane Precipitation Foam," presented at the 156th National Meeting, ACS, Atlantic City, N. J., Sept. 8-14, 1968.

5. W. D. Ross and R. T. Jefferson, J. of Chromatogr. Sci. 8, 386 (1970).

6. I. O. Salyer, R. T. Jefferson, and W. D. Ross, U. S. Patent 3,580,843, May 28, 1971.

7. F. D. Hileman, R. E. Sievers, G. G. Hess, and W. D. Ross, Anal. Chem. 45, 1126 (1973).

8. L. C. Hansen and R. E. Sievers, J. of Chromatogr. 99, 123 (1974).

9. T. R. Lynn, D. R. Rushneck, and A. R. Cooper, J. of Chromatogr. Sci. 12, 76 (1974).

10. J. D. Navratil and R. E. Sievers, Am. Lab. 9, 38 (1977).

11. J. D. Navratil, R. E. Sievers, and H. F. Walton, Anal. Chem. 49, 2260 (1977).

12. C. M. Smith and J. D. Navratil, Separation Science and Technology 14, 255 (1979).

13. Standard Methods for the Examination of Water and Wastewater, 510C, 14 ed., American Public Health Association, American Water Works Association, and Water Pollution Control Federation, (M. H. Franson, ed.), Washington, D. C., 1975, p. 580.

14. W. D. Ross, Monsanto Research Corporation, Dayton, Ohio, personal communication, July 1978.