

Synthesis, Characterization, and Applications of Condensate Porous Polymeric Sorbents Based on *m*-Phenylenediamine

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Synopsis

A few condensate porous polymeric sorbents were synthesized based on *m*-phenylenediamine-melamine-formaldehyde polycondensation using suitable porosogenic agents. They were characterized for ion-exchange capacity, bulk density, solvent uptake, pH-titration curve, and rate of exchange. Their surface characteristics were studied using mercury porosimetry, scanning electron microscopy, and the uptake of fast green FCF dye. A selected sorbent was studied for the uptake of phenol in static and dynamic conditions, and the uptake performance was compared with commercially available porous anion exchanger Amberlite-IRA 93. Results obtained clearly indicated that modified products have higher pore volume, higher surface area, and good ion-exchange kinetics as compared to the conventional gel type product.

INTRODUCTION

Helfferich¹ has given an exhaustive survey of conventional condensate gel type products which are having adsorption and ion-exchange properties. These products have been exhaustively studied, and they played valuable role in many fields. However, these conventional sorbents lacked true porosity, adequate surface area, superior dimensional stability, faster rate of uptake, and nonfouling type of matrix so as to be more fruitfully useful as regenerable sorbents. Modified polymerization techniques have resulted in three-dimensionally crosslinked porous polymeric sorbents of both addition^{2,3} and condensation⁴ type, which have overcome the above-mentioned drawbacks. Condensate porous polymeric sorbents have shown equally good or sometimes better application potentials than those of porous addition type^{5,6} sorbents. Literature survey showed scanty published work on porous condensate sorbents based on *m*-phenylenediamine. Samborski et al.⁷ prepared a porous ion exchanger by cocondensation of *m*-phenylenediamine, phenol, and formaldehyde in acid medium. Kishima⁸ reported a porous condensate ion-exchange resin in bead form derived from polycondensation of *m*-phenylenediamine in a mixture of dialkylphthalate and carbon tetrachloride. Kodoike⁹ reported a process whereby the surface area of the *m*-phenylenediamine-formaldehyde condensation product could be increased by the addition of silicic acid. However, no condensate porous sorbent based on the reaction of *m*-phenylenediamine-melamine is reported. This publication deals with an attempt to synthesize, characterize, and assess the application potential of a few such condensate porous sorbents.

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EXPERIMENTAL

Reagents. The following chemicals of laboratory reagent grade were used: *m*-phenylenediamine, melamine, formaldehyde as 37% aq solution, hydrochloric acid, methanol, 1-pentanol, hexanol, octanol, decanol, cyclohexanol, petroleum ether, 1-heptane, 2-octane, decane, benzene, toluene, xylene, cyclohexane, starch, and ammonium hydroxide. The following chemicals of AR grade were used. Phenol, methanol, 4-amino antipyrine, potassium ferricyanide, ammonium chloride, sodium thiosulfate, potassium bromide, potassium bromate, potassium iodide, and 2,6-dibromoquinone chlorimide. Amberlite IRA-93, a weak base porous anion exchanger supplied by Rohm and Haas Co., Philadelphia, was studied for comparison.

Synthesis. A generalized procedure for the preparation of a condensate porous polymeric sorbent based on *m*-phenylenediamine was used. Exactly 0.1 mol of *m*-phenylenediamine was dissolved in a suitable quantity of water in a round-bottom three-neck flask fitted with a stirrer, a thermometer, and a condenser; to this an appropriate quantity of concentrated hydrochloric acid (10*N*) and a suitable porosogenic agent was added, and the mixture was cooled to 0–5°C. In another similar round-bottom three-neck flask an appropriate quantity of melamine and formaldehyde were warmed to 60–70°C with stirring till a clear solution was formed. This solution was also cooled to 0–5°C and was added, drop by drop, to the above-mentioned cold solution of *m*-phenylenediamine with stirring and maintaining the temperature at 0–5°C. After the addition, an exothermic reaction took place, and within a few minutes a black gel was formed. The gelled mass was removed, cured at 115–120°C for 3 h, cooled and crushed to –18, +52 BSS mesh size. The sieved resin was then stored until needed.

Following this generalized procedure, a series of condensate porous sorbents were prepared. Polymeric sorbents synthesized were designated as: (1) MFM–MT, (2) MFM–PT, (3) MFM–HX, (4) MFM–OT, (5) MFM–DT, (6) MFM–CX, (7) MFM–PTE, (8) MFM–HPT, (9) MFM–OCT, (10) MFM–DCT, (11) MFM–CHX, (12) MFM–BZ, (13) MFM–TU, (14) MFM–XY, and (15) MFM–C. Here the first M stands for *m*-phenylenediamine, F for formaldehyde, and the second M for melamine. The letters after MFM stand for the porosogenic agents used as given in Table II.

First a series of polycondensation reactions were carried out to find out the effect of melamine content on the characteristics of the finished products. These were conventional gel products prepared in the absence of any porosogenic agent. Selecting the optimum ratio of the quantity of *m*-phenylenediamine to melamine based on the ion-exchange capacity and the bulk density of finished products, a series of porosogenic agents were used for the preparation of condensate porous polymeric sorbents in the ratio of the quantity of the total condensate to that of the porosogenic agent as 1:1 (w/w). Keeping the optimum ratio of the quantity of *m*-phenylenediamine to that of the melamine, and selecting one porosogenic agent which gave an optimum ion-exchange capacity and bulk density to the end products, an exhaustive study of the effect of variation of the ratio of the quantity of the total condensate to that of the porosogenic agent on characteristics of resulting polymeric sorbents was carried out. Finally, keeping all optimum conditions constant, a series of batches were made to check the reproducibility of characteristics of condensate porous polymeric sorbents.

Characterization. All adsorbents synthesized were typical weakly basic anion exchangers. The ion-exchange capacity and bulk density were determined by standard methods.¹⁰ Values given for ion-exchange capacity are reproducible to the second decimal place and for bulk density to fourth decimal place. Out of these sorbents one, namely, MFM-PT, was selected for further exhaustive study. For pH-titration study (Ref. 10) and solvent uptake standard methods¹¹ were followed. Values for the solvent uptake are reproducible to the second decimal place. For the rate of ion-exchange study the method described in previous publication was followed.¹² Porosity and surface area were determined by mercury porosimetry^{13,14} using Aminco 60,000 psi Model Mercury Porosimeter manufactured by the American Instrument Co., Division of Travenol Laboratories, Inc. (8030 Georgia Avenue, Silver Spring, MD 20910). Porosity was also determined by the uptake of Fast Green FCF dye following the procedure recommended by Abrams.¹⁵ These values are reproducible to the first decimal place. A surface morphology study of these condensate porous sorbents was carried out using a Cambridge Stereoscan S4-10 Scanning Electron Microscope manufactured by Cambridge Scientific Instruments, Ltd., Cambridge, England. The procedure adopted for sample preparation is briefly outlined below. One side of a double sided adhesive tape was fixed on the metal stub, and on the other side powder of polymer was spread to form a thin layer. To make the specimen conducting while examining in the scanning electron microscope, colloidal silver paint was applied on the edge of the stub, and the specimen was subsequently coated with a thin layer of gold (200–300 Å thickness) by vacuum evaporation.

Phenol Uptake. The effect of the concentration of the equilibrated aqueous phenol solution on its uptake by porous polymeric adsorbent was studied. Preliminary experiments indicated that a period of 24 h was sufficient for attaining an equilibrium. 50 mL of aqueous solutions of phenol having different concentrations were equilibrated with 0.5 g of polymeric sorbent in each of a series of 150-mL-capacity stoppered conical flasks for a period of 24 h at 30°C with continuous shaking. Supernatant solutions were decanted and analyzed for the residual phenol by the bromination method.¹⁶ Values are reproducible to the second decimal place. Polymeric sorbent was simultaneously evaluated for the moisture content.

The polymeric sorbent MFM-PT and the commercially available anion exchanger Amberlite IRA-93 were converted to Cl⁻ form and polymer beds, each of the 10.0-mL bed volume and 12.5-cm bed height, were assembled and a 50-ppm aqueous solution of phenol was passed through beds separately at a flow rate of 10 bed volumes/h until the breakthrough point. To prevent the oxidation of phenol, the method suggested by Show¹⁷ was followed. The first appearance of phenol in the effluent from polymer beds, as tested by Gibb's method,¹⁸ was considered as the breakthrough point. Effluent was collected in suitable fractions and analyzed by the colourimetric method (Ref. 16, p. 31). Beds were rinsed with double distilled water till there was no phenol in the washing. The elution was carried out with 2% sodium hydroxide solution prepared in 1:1 water-methanol mixture at a flow rate of 3 bed volumes/h. The eluant fractions of 5 mL volume each were collected and evaluated for the phenol content. During the loading as well as the elution cycle, void volume was rejected. In the case of MFM-PT porous polymeric sorbent, the experiment was repeated exactly

TABLE I
Effect of the Variation of the Ratio of the Quantity of *m*-Phenylenediamine to That of the Melamine on Characteristics of Polymeric Sorbents Based on Them

Sample no.	Moles of <i>m</i> -phenylene-diamine	Moles of melamine	Bulk density (g·cm ⁻³)	Ion-exchange capacity (meq·g ⁻¹)
1	1.00	1.00	0.6945	3.89
2	1.00	0.75	0.6757	4.22
3	1.00	0.50	0.6580	3.95
4	1.00	0.25	0.6410	4.20
5	1.00	2.00	0.6619	3.78
6	1.00	4.00	0.6523	4.06

in the same manner to check the reproducibility of results, after converting the sorbent to Cl⁻ form. Similarly, methanol alone was also used as an eluant following the procedure outlined above.

RESULTS AND DISCUSSION

Synthesis

Since sorbents should be insoluble and infusible under a wide spectrum of experimental conditions, a three-dimensionally crosslinked structure is required. For this purpose monomers should be polyfunctional. Literature survey does not show any concrete relationships between the nature of the porosogenic agent

TABLE II
Effect of the Nature of the Porosogenic Agent on Characteristics of Porous Polymeric Sorbents Based on *m*-Phenylenediamine and Melamine^a

Sample no.	Porosogenic agent	Name of the sorbent	Bulk density (g·cm ⁻³)	Ion-exchange capacity (meq·g ⁻¹)
1	Methanol	MFM-MT	0.7142	3.49
2	1-Pentanol	MFM-PT	0.3847	3.49
3	Hexanol	MFM-HX	0.4879	3.53
4	Octanol	MFM-OT	0.3892	3.64
5	Decanol	MFM-DT	0.3988	3.94
6	Cyclohexanol	MFM-CX	0.4515	4.10
7	Petroleum ether	MFM-PTE	0.6648	4.24
8	1-Heptane	MFM-HPT	0.6832	4.05
9	2-Octane	MFM-OCT	0.6342	4.03
10	Decane	MFM-DCT	0.6348	4.40
11	Cyclohexane	MFM-CHX	0.5989	3.82
12	Benzene	MFM-BZ	0.5555	3.93
13	Toluene	MFM-TU	0.5519	3.92
14	Xylene	MFM-XY	0.5564	4.01
15	(Conventional matrix)	MFM-C	0.6410	4.20

^a Molar ratio of *m*-phenylenediamine:melamine:formaldehyde = 1:0.25:5.5. Ratio of total condensate to porosogenic agent = 1:1 (w/w).

TABLE III
Effect of the Variation of the Ratio of the Quantity of the Total Condensate to That of the Porosogenic Agent on Characteristics of Condensate Porous Sorbents Based on *m*-Phenylenediamine and Melamine^a

Sample no.	Ratio of total condensate to porosogenic agent (w/w)	Bulk density (g·cm ⁻³)	Ion-exchange capacity (meq·g ⁻¹)
1	1:1	0.3847	3.49
2	1:2 ^b	0.3021	—
3	1:0.75	0.4345	3.60
4	1:0.50	0.5642	3.90

^a Molar ratio of *m*-phenylenediamine:melamine:formaldehyde = 1:0.25:5.5. Porosogenic agent = 1-pentanol.

^b Dimensional stability of the sorbent was very poor and hence was not evaluated for the ion-exchange capacity.

and its quantity on one hand and the porosity realized in the resulting condensate product on the other hand; hence a trial-and-error approach is necessary in the selection of the porosogenic agent. The duration for the attainment of gelation stage and characteristics of end products vary depending on the ratio of the quantity of *m*-phenylenediamine, melamine, and formaldehyde (Table I), the nature of the porosogenic agent (Table II), and the ratio of the quantity of the porosogenic agent to that of the total condensate (Table III). At the time of gelling, the entire reaction mixture forms an expanded spongy mass. In all probability in these cases the polymer matrices consist of units corresponding to conventional polymers encasing discrete diluent cells which, in fact, must be appearing as pores so these porous condensate polymers have both discrete pores and gellular structures (Ref. 15).

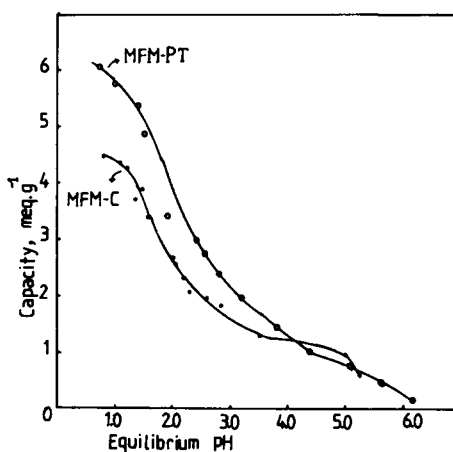


Fig. 1. pH-Titration curve of condensate porous polymeric sorbents, MFM-PT: Quantity of sorbents, 0.5 g; equilibration temperature, 30°C; equilibration period, 24 h; solutions used, (a) 0.1N HCl in 1.0N NaCl and (b) 1.0N NaCl.

Characterization

As already stated above, characteristics of condensate porous polymeric sorbents are the resultant effect of many governing parameters adopted during the condensation polymerization.

Ion-Exchange Characteristics. There appears no possibility of generalizing the effect of the nature of the porosogenic agent on the bulk density of end products. Higher aliphatic alcohols reduce bulk density appreciably (Table II), but no relationship between the chain length of the alcohol and the value of the bulk density could be established. The greater the ratio of the quantity of the total condensate to that of the porosogenic agent the lower is the bulk density (Table III). However, bulk density indicates the porous nature of the matrix.¹⁹

As a typical characteristic of a weak base anion exchanger, the condensate polymeric sorbent show relatively good ion-exchange capacity at lower pH values (Fig. 1). The quantity of the crosslinking agent used has not affected the ion-exchange capacity appreciably (Table I). No relationship emerges between the porosity of the matrix and the corresponding ion-exchange capacity (Table II). In some modified matrices, even though the bulk density is more (i.e., less porous nature of the matrix) than that of the conventional unmodified matrix, ion-exchange capacity is more. While in majority of products bulk density is less, indicating porous nature of the matrix but the ion-exchange capacity is also less. This may be due to the reason that not only the porosity but pore size distribution must also be a deciding factor in the realization of ion-exchange capacity. If the porosity attained is due to pores of bigger size, then the internal surface accessible is comparatively less, resulting in less ion-exchange capacity. This is obvious because in such a case diffusion inside polymer matrix is not that facile. A perusal of the trends of the rate of ion-exchange (Fig. 2) clearly indicates that the rate of exchange is fast with porous sorbent as compared to that of the conventional sorbent.²⁰ For MFM-C only 19.05% of its total capacity is realized in the first 10 min as against 33.07% for MFM-PT.

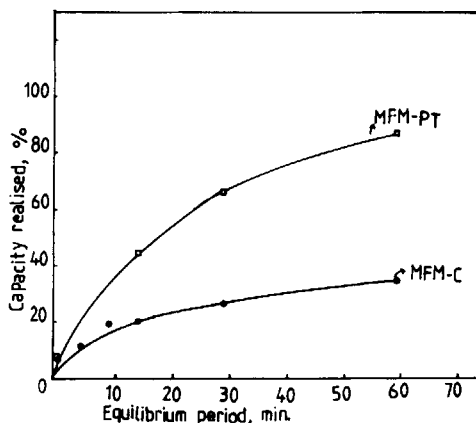


Fig. 2. Rate of exchange of condensate porous polymeric sorbent, MFM-PT: Quantity of sorbent, 0.5 g; equilibrating solution, 0.1N sodium hydroxide; volume of the equilibrating solution, 50 mL; equilibration temperature, 30°C.

TABLE IV
 Reproducibility of Characteristics of Condensate Porous Polymeric Sorbents Based on *m*-Phenylenediamine and Melamine Using 1-Pentanol as the Porosogenic Agent^a

Batch no.	Bulk density (g·cm ⁻³)	Ion-exchange capacity (meq·g ⁻¹)
1	0.3847	3.49
2	0.3899	3.48
3	0.3852	3.48
4	0.3839	3.50

^a Molar ratio of *m*-phenylenediamine:melamine:formaldehyde = 1:0.25:5.5. Ratio of the total condensate:porosogenic agent = 1:1 (w/w).

Surface Characteristics. A solvent uptake study gives some idea about the porous nature of the matrix. In general, the more the porosity, the more the solvent uptake (Table V). Solvent uptake study clearly supports the conclusions arrived at by the study of the bulk density.

Abrams¹⁵ states that the following parameters affect the adsorptivity of condensate porous polymeric adsorbents for Green Dye FCF: (1) chemical nature of the matrix, (2) nature of the functional groups, (3) polarity of the matrix, (4) hydrophilicity of the matrix, (5) particle size, and (6) physical characteristics such as surface area, porosity, pore size, etc. Out of these parameters, except the last one, all others are constant for polymeric sorbents synthesized. The green dye uptake is profoundly influenced by physical characteristics like surface area, porosity, pore size, etc. For example, the percent adsorptivity after 1 h is nil for MFM-C, a conventional sorbent as against 65% for MFM-PT, a porous matrix (Table V). This percent adsorptivity value compares fairly well with that of commercially available adsorbent Duolite-ES 111 (say 72%¹⁵).

Data obtained by mercury porosimetry (Table VI) clearly distinguishes between a gel-type matrix and a porous matrix. For a gel-type matrix MFM-C the maximum contribution towards total pore volume is due to pores of large diameter, and, consequently, it shows poor surface area (say 6.92 m²/g). On the other hand, in the case of modified matrix MFM-PT, 17.3% of the total porosity is due to smaller pores, and hence this matrix shows comparatively more surface area (say 38.89 m²/g).

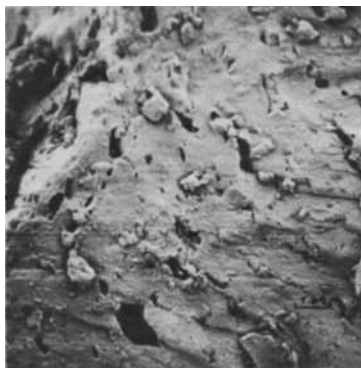


Fig. 3. Scanning electron microphotograph of MFM-C (6100 × magnification).

TABLE V
 Characteristics of Condensate Porous Polymeric Sorbents, MFM-PT

Poly- meric sorbent	Ion-exchange capacity ($\text{meq}\cdot\text{g}^{-1}$)	Wet absolute density ($\text{g}\cdot\text{mL}^{-1}$)	Bulk density ($\text{g}\cdot\text{cm}^{-3}$)	Cyclo- hexane uptake ($\text{g}\cdot\text{g}^{-1}$)	Dye uptake (% absorptivity) 1 h 24 h	Porosity ($\text{mL}\cdot\text{g}^{-1}$)	Surface area ($\text{m}^2\cdot\text{g}^{-1}$)	Average pore diameter (\AA)
MFM-C	4.20	1.19	0.6410	0.0317	Nil	0.1538	6.92	889
MFM-PT	3.49	1.11	0.3847	0.2740	65.0 89.9	0.4916	38.89	505

TABLE VI
Pore Size Distribution of Condensate Porous Polymeric Sorbent, MFM-PT

Polymeric sorbent	Total porosity (mL·g ⁻¹)	Equivalent pore diameter (μm)	% Porosity contribution
MFM-C	0.1538	100.56-0.0973	91.48
		0.0637-0.0040	8.52
MFM-PT	0.4916	82.19-0.1130	83.70
		0.0818-0.0034	17.30

Scanning electron micrographs (SEM) provide very good information about the surface morphology of sorbents. SEM of MFM-C a conventional gel type matrix (Fig. 3) shows a highly smooth surface with a continuous polymer phase. SEM of MFM-PT a porous matrix (Fig. 4) indicates a heterogenous nature of the matrix with small and big pores unevenly distributed throughout the surface.

Uptake of Phenol. Literature survey²¹ shows that phenol uptake by polymeric sorbents involves both the matrix and the functional groups. When MFM-C and MFM-PT sorbents are considered, the nature of functional groups is the same. This leaves only the concentration of ionogenic groups (i.e., ion-exchange capacity) and the nature of the matrix to be considered for offering explanation for the phenol uptake. The nature of the matrix involves its chemical composition and the surface characteristics like porosity, pore size distribution, and surface area. For both sorbents chemical composition of the matrix is the same. So the difference in the uptake could only be explained on the basis of ion-exchange capacity and surface characteristics. The higher uptake of phenol by the porous matrix MFM-PT (Table VII) as compared to that of the conventional gel-type matrix MFM-C is certainly due to higher porosity and surface area of the former matrix.

The uptake of phenol by the porous polymeric sorbent MFM-PT is influenced by the concentration of the equilibrated solution (Table VII). The uptake increases rapidly in the lower concentration range, but, as the concentration in-



Fig. 4. Scanning electron microphotograph of MFM-PT (6100 × magnification).

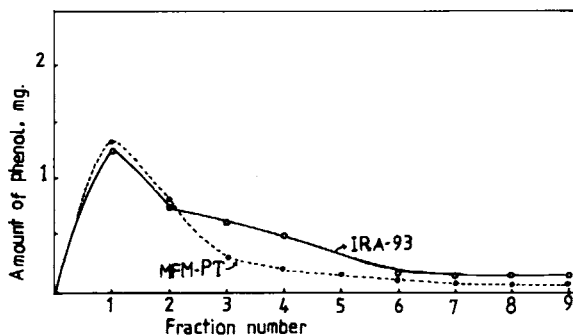


Fig. 5. Elution of phenol from polymeric sorbents using methanol as eluant. Total quantity of phenol loaded: (a) MFM-PT, 5.25 mg; (b) Amberlite, IRA 93, 7.51 mg; eluant, methanol; elution flow rate, 3 bed vol/h; fraction volume, 5 mL.

creases, a stage is reached beyond which the uptake becomes independent of equilibrium concentration and assumes more or less constant value.

Under dynamic conditions also the condensate porous adsorbent MFM-PT shows good uptake of phenol. It treats 10.5 bed volume of 50 ppm aqueous phenol solution up to the breakthrough point at service flow rate of 10 bed vol-umes/h (Table VIII).

Methanol elution removes only 3.11 mg of phenol out of 5.25 mg taken up in the case of MFM-PT sorbent in about 4.5 bed volumes and trailing phenomenon is predominant (Table IX, Fig. 5). The same thing is observed with Amberlite IRA-93 wherein 3.85 mg phenol could be removed in 4.5 bed volumes out of 7.51

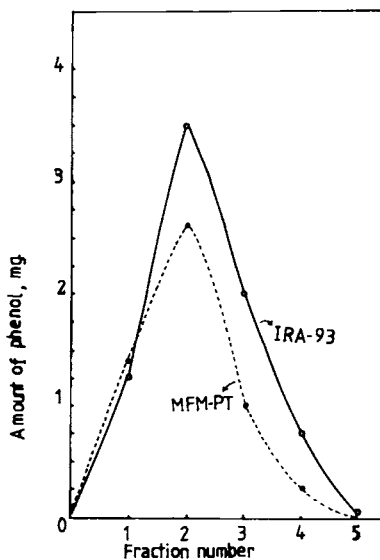


Fig. 6. Elution of phenol from polymeric sorbents using 2% sodium hydroxide in 1:1 water:methanol. Total quantity of phenol loaded: (a) MFM-PT, 5.25 mg; (b) Amberlite, IRA 93, 7.50 mg; eluant, 2% sodium hydroxide in 1:1 water:methanol; elution flow rate, 3 bed vol/h; fraction volume, 5 mL.

TABLE VII
Effect of the Initial Concentration of Phenol on Its Uptake by the Condensate Porous Polymeric Sorbent, MFM-PT^a

Initial concentration of phenol in aq solution (ppm)	Uptake of phenol (mg·g ⁻¹) (absolute dry)
36.36	0.30
72.72	1.06
90.90	6.91
145.40	9.61
181.80	12.02
694.00	31.54
1080.00	43.46
1456.00	52.42
1818.00 ^b	59.32
4122.00	126.10
9064.00	250.00
10000	250.00

^a Quantity of the equilibrated sorbent, 0.5 g (air dry); volume of the equilibrated solution, 50 mL; equilibration temperature, 30°C; equilibrium period, 24 h.

^b Under exactly similar conditions the condensate gel type of sorbent, MFM-C showed 45.12 mg/g uptake of phenol.

TABLE VIII
Uptake of Phenol by Condensate Porous Polymeric Sorbent, MFM-PT under Dynamic Conditions^a

Sorbent	Quantity of the solution treated up to the break-through point (bed volumes)	Quantity of phenol taken up (mg)
MFM-PT	10.5	5.25
Amberlite IRA 93	15.0	7.5

^a Bed volume, 10 mL; influent, 50 ppm aq solution of phenol; flow rate, 10 bed volumes/h.

TABLE IX
Elution of Phenol from the Polymer Matrix under Dynamic Conditions^a

Sorbent	Cycle no.	Quantity of phenol loaded (mg)	Quantity of phenol eluted out (mg)		% Elution
			Methanol	2% NaOH in 1:1 methanol	
MFM-PT	I	5.25	—	5.25	100
	II	5.26	—	5.25	99.8
	III	5.25	3.11	—	59.23
Amberlite IRA 93	I	7.50	—	7.50	100
	II	7.51	3.85	—	51.26

^a Bed volume = 10 mL; influent = 50 ppm aq solution of phenol; loading flow rate = 10 bed volumes/h; elution flow rate = 3 bed volumes/h.

mg total loading. This indicates that a part of the phenol uptake appears to be by molar sorption and the remaining by ion exchange. When alcoholic sodium hydroxide is used as an eluant, the entire amount of loaded phenol is eluted out in 2.5 bed volumes of the eluant (Fig. 6). About 90% and 97% of the loaded phenol is eluted out in 1.5 bed volumes of this eluant in the case of Amberlite IRA-93 and MFM-PT, respectively.

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