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TECHNICAL NOTE

Preconcentration and Separation of Phenols from Water by Polyurethane Foams

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ABSTRACT

The application of untreated and polyurethane foams treated with tributylphosphate (TBP) in the preconcentration of some phenols from water via static and flow experiments was carried out. Batch experiments with the TBP-loaded foams showed a good affinity toward extraction of the tested compounds as compared to the untreated foams. The use of the unloaded and TBP loaded foams was also employed in column modes for the preconcentration of the phenols used. The effect of extraction media, phenol concentration, time of shaking, temperature, sample volume, ionic strength, eluting solvent, and flow rate on the retention efficiency of the compounds by the foam were investigated. The extraction efficiency and the recovery of the compounds from the foam material by the column were obtained up to 100%. Sorption of the compounds by the foam was brought by a solvent extraction mechanism. The pK_a and the molecular weight of the absorbates play an important role in the sorption process. The height equivalent to

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theoretical plates (HETP) for the foam column were obtained from the Glueckauf equation and the breakthrough capacity curve, and were found to equal 1.8–2.05 mm at flow rates up to 10 $cm^3 \cdot min^{-1}$. Attempts were also made to separate some of the tested phenols by dynamic techniques.

Key Words. Polyurethane foam; Phenols; Preconcentration; Recovery; Tributylphosphate

INTRODUCTION

Phenol and phenol-like compounds represent a class of man-made environmental pollutants which also occur naturally in the environment (1). The presence of these compounds in the wastewater of chemical factories often represents a risk to the environment (2, 3). The main sources of these species are combustion processes, chemical factories, and industrial and sewage effluents (3, 4). The occurrence of such compounds in the aquatic environment has been known to cause severe health problems to animals, birds, and humans (5, 6). The removal or reduction of these pollutants to an acceptable concentration by extraction with organic solvents, steam distillation, oxidation reaction, adsorption on carbon, reversed liquid–liquid partition filter chromatography, or the use of cellulose triacetate membrane filters has been investigated (7–11). Such preconcentration techniques are often slow or cumbersome, limited by a relatively low flow rate (0.65 $cm^3 \cdot min^{-1}$), and too expensive for routine work where many large volume samples are concentrated on-site prior to quantitative analysis (10).

Recently, several authors have proposed open cell polyurethane foam as an inexpensive solid extractor and effective sorbent for the removal of water pollutants (12–18). The solid foam concentrates various species in solution by the phase distribution mechanism rather than adsorption (12, 13). The membrane-like structure of the foams together with the efficient sorption properties offer many advantages over other solid collectors as they allow a higher concentrating ability compared with other solid materials which depend only on adsorption (19, 20).

The present work deals with the use of polyurethane foam for the extraction of some phenols from high volume samples of aqueous media in an attempt to establish the conditions where good extraction and recoveries of these compounds could be obtained.

EXPERIMENTAL

Reagents and Materials

All chemicals used were of analytical reagent grade. Polyurethane foam, an open polyether type (bulk density 30 kg·m^{-3}), was supplied by K.g. Schaum (Stoffwerk, Kremsmunster, Austria). The foam, loaded with tributylphosphate (TBP), was prepared by mixing the dried foam cubes with 2% TBP in benzene (10 cm^3·g^{-1} dry foam) with stirring for 15 minutes. The reagent foam was then dried (12). The compounds tested were phenol, *o*-chlorophenol, *o*-nitrophenol, *m*-cresol, *p*-cresol, resorcinol, and salicylaldehyde. A stock solution of each compound containing 100 μg·cm^{-3} was prepared in a 100-cm^3 measuring flask by dissolving the exact weight of the compound in distilled and/or tap water. A series of standard solutions of these compounds was prepared by diluting their stock solutions with water. All solutions were stored in polyethylene bottles.

Apparatus

A double-beam spectrophotometer, Varian DMS 634 with a 1-cm quartz cell, was used for the absorbance measurements. An Orion pH meter and glass columns, 12 cm × 10 mm i.d., were also used.

GENERAL PROCEDURES

Batch Experiments

To investigate the effect of shaking time on the uptake of the compounds on polyurethane foam, the foam cubes (0.3 g) were equilibrated with a 100-cm^3 solution of each compound (60 μg·cm^{-3}) in separate polyethylene bottles and shaken for various time intervals up to 1 hour. The foam cubes were then separated by decantation, and the amount of the compound remaining in solution was measured spectrophotometrically at the wavelength of maximum absorption. The amount of compound retained on the foam was calculated by difference. Following these procedures, the effects of extraction media, phenol concentration (10–80 μg·cm^{-3}), ionic strength, pH, and temperature on the extraction efficiency were determined.

Flow Experiments

In the flow of experiments, 1 g of dry foam was packed into the column using the vacuum method of foam packing (12). Tap or distilled water

(1–3 dm^3) samples containing 0.2 mg of each compound were passed through the foam column at 10–15 $cm^3 \cdot min^{-1}$. After squeezing water from the foam material, the compound was recovered from the foam with 100 cm^3 ethanol in a Soxhlet extractor. The sample was determined by measuring the absorbance of the solution against a reagent blank. Following these procedures, the effect of eluting solvent and flow rate on the extraction were also determined.

RESULTS AND DISCUSSION

The introduction of porous polyurethane foam as a cellular solid extractant for high volume water samples has been proven advantageous due to its easy handling and clean-up and its high ability to sorb many different organic and inorganic species (12, 13). The polyurethane foam method allows the isolation of the analyte from the matrix and yields an appropriate enrichment factor. The excellent hydrodynamic properties of the foam column allow the application of quite high flow rates without the need to use vacuum, while the rapid attainment of sorption equilibrium in the thin membranes forming the foam material reduces the time required for analysis.

Preliminary experiments using unloaded and TBP-loaded polyurethane foam have shown that the extraction of the investigated compounds is rapid and equilibrium is reached in less than 1 hour, followed by a plateau. Hence, a minimum of 1 hour was used in obtaining the extraction isotherms. The results obtained are summarized in Fig. 1. A good extraction efficiency was obtained with the TBP-treated foam (Fig. 1a) as compared to the unloaded foam (Fig. 1b).

Extraction Isotherm

The uptake of the investigated compounds from aqueous solution by the unloaded and TBP-loaded foams was found to depend on its concentration. Thus, in separate experiments the extraction isotherms were developed over a wide range of equilibrium concentrations (10–80 $\mu g \cdot cm^3$) for each compound. The pH values of the aqueous solutions in these experiments were selected (>5, Ref. 6) so that the compounds are predominantly in undissociated foams. The isotherms of the tested compounds exhibited a first-order behavior in the low concentration range and tended to plateau at high bulk solution concentrations, as shown in Fig. 2. The sorption of the different phenolic compounds by the unloaded foams (Fig. 2a) increases in the order *o*-nitrophenol < *o*-chlorophenol < phenol < *m*-cresol < *p*-cresol < resorcinol < salicylaldehyde. Similar trends were

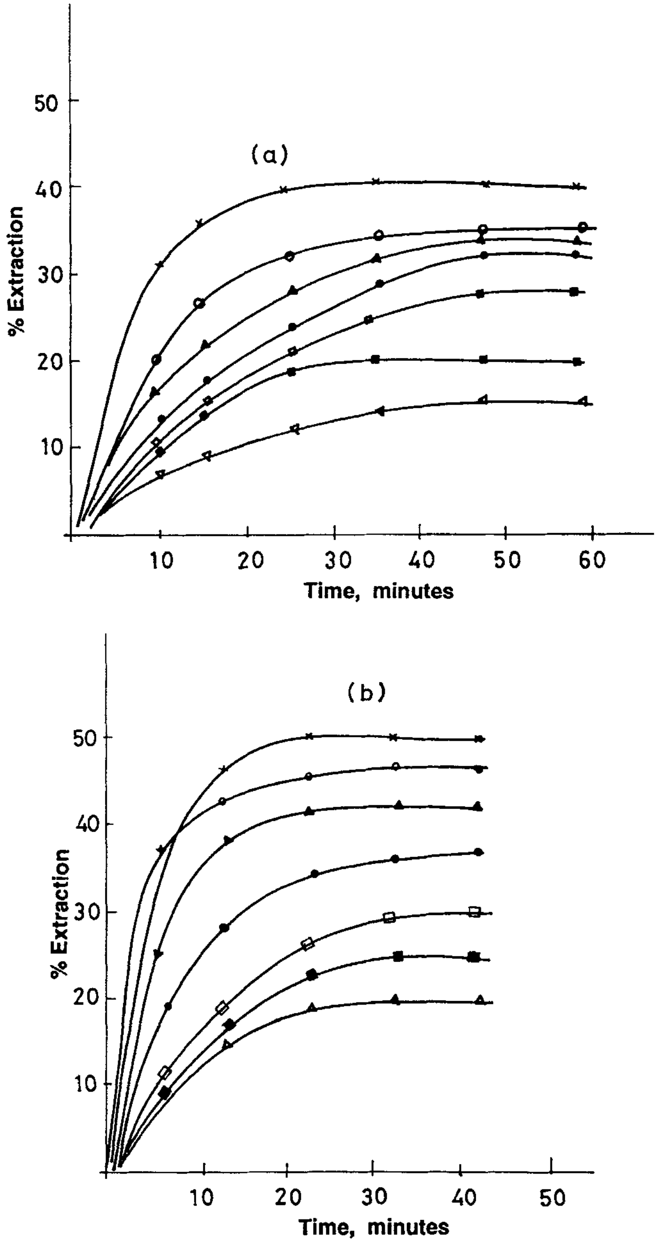

FIG. 1 Effect of shaking time on the extraction of the compound tested with unloaded (a) and TBP-loaded foams (b). (×) Resorcinol, (○) salicylaldehyde, (▲) *p*-cresol, (●) *m*-cresol, (□) phenol; (■) *o*-chlorophenol, and (△) *o*-nitrophenol.

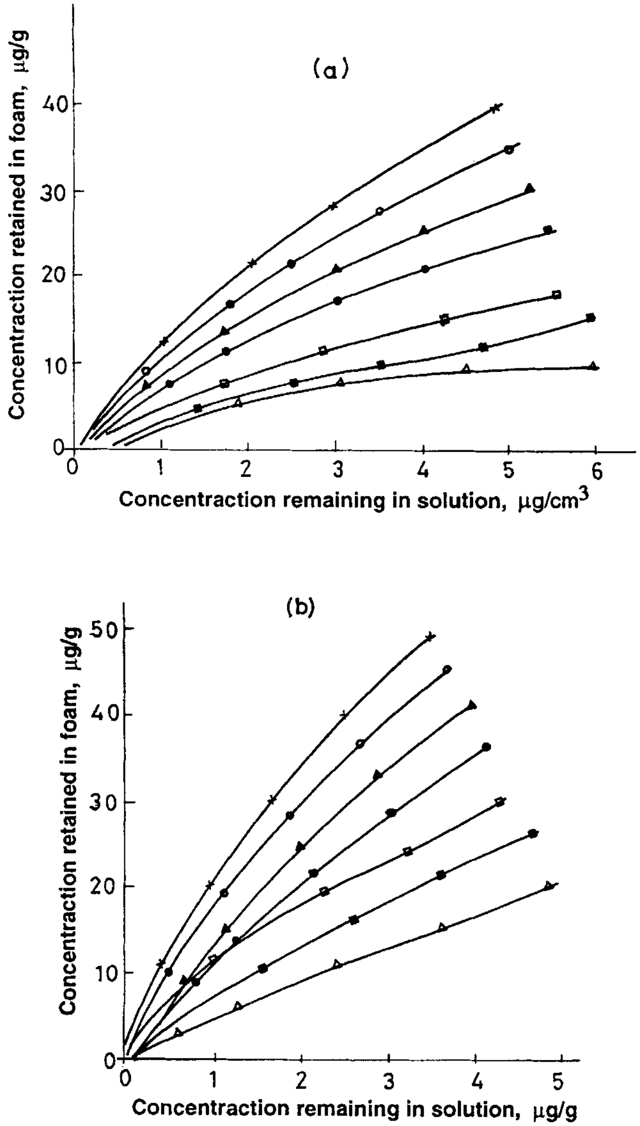

FIG. 2 Extraction isotherms of the compound tested with unloaded (a) and TBP-loaded foams (b). (×) Resorcinol, (○) salicylaldehyde, (▲) *p*-cresol, (●) *m*-cresol, (□) phenol, (■) *o*-chlorophenol, and (△) *o*-nitrophenol.

obtained with TBP-loaded foams (Fig. 2b). Therefore, a solvent extraction mechanism is the most probable for the extraction of these compounds by the untreated foams, and an anion-exchange mechanism is completely excluded. This was confirmed by investigating the extraction of these compounds with ether. The sequence of the extraction efficiency was found to be similar to that obtained by unloaded and TBP-loaded foams. It is worth noting that the extraction percentage depends on the pK_a (Table 1) of the absorbate. The molecular weight of the absorbate and hydrogen bonding are also participating factors in the extraction. However, these results do not agree with the general understanding that the larger the molecular weight of the absorbate, the larger the amount extracted when the substances concerned are similar in nature (21).

The effect of temperature on the extraction efficiency of the unloaded and TBP-loaded foams were determined at 35, 45, and 55°C. Similar trends of TBP-loaded and unloaded foams were obtained, and the percentage sorption increased slightly with increasing temperature. Discrepancies were observed in the case of *o*-nitrophenol, which has a higher acidity and molecular weight, where the percentage extraction is highly increased as compared to the other phenols.

The influence of the pH of the aqueous phase on the extraction of each of the compounds tested (60 $\mu g \cdot cm^3$) by the unloaded foams was examined over the pH range 3–11 by measuring the absorbance of the aqueous phase after extraction. The sorption profiles of the investigated compounds are given in Fig. 3, from which it can be seen that the percentage removal of

TABLE 1
Extraction and Recovery of the Compound Tested (0.2 mg) from 3 L Aqueous Solutions by the Proposed Unloaded Foam Column at 8–10 $cm^3 \cdot min^{-1}$[a]

		% Recovery[b]		
Compound	pK_a	a	b	Wavelength
Phenol	9.9	100	102.1	265
Resorcinol	9.8	98	95	276
o-Chlorophenol	8.5	97	99	274
o-Nitrophenol	7.17	99	93	346
m-Cresol	10.1	96	98	272
p-Cresol	10.2	98	99	280
Salicylaldehyde	10	99	102.1	257

[a] Average of three data from distilled water (a) and from Nile river water (b).

[b] Poor recoveries were obtained with ethanol.

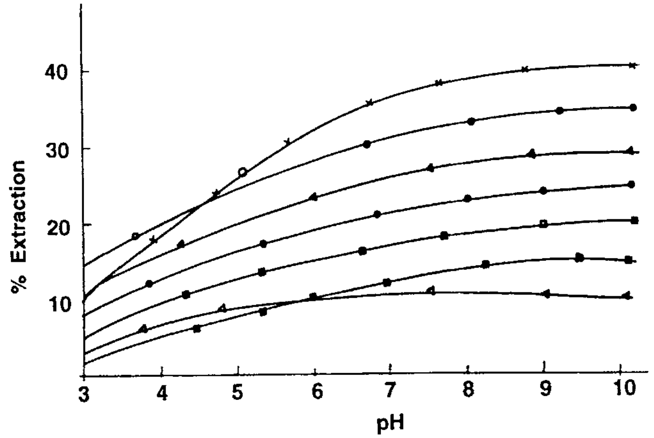

FIG. 3 Effect of pH on the extraction of the compound tested with unloaded foams. (×) Resorcinol, (○) salicylaldehyde, (▲) *p*-cresol, (●) *m*-cresol, (□) phenol, (■) *o*-chlorophenol, and (△) *o*-nitrophenol.

the compounds increases markedly with increasing pH and reaches a plateau at pH ≃ 10. The pH values were adjusted with HCl or NaOH. The addition of sodium chloride (0.01–0.1 M) did not increase the amount of compound extracted in any system.

The influence of ethanol (0–10%) on the extraction efficiency of the compounds tested was examined with two selected compounds, phenol and resorcinol, by the unloaded foams. The sorption profiles of the compounds tested are given in Fig. 4. It has been found that extraction of the compounds by the foams is generally decreased by the addition of ethanol to the aqueous phenolic compound solution. This is probably due to formation of a lipophilic association in the aqueous solution (22). These data are in agreement with the suggestion of Kirkwood (19) that the smaller the dielectric constant, the larger the amount extracted. Thus, the nature of the media has a marked effect on sorption characteristics.

Dynamic Experiments

The results obtained for the extraction properties of the compounds tested in aqueous solution with unloaded polyurethane foam suggest the possible application of polyurethane foam in the column extraction mode for the quantitative collection and recovery of these compounds from aqueous media. Distilled or tap water samples (0.1–3 dm^3) containing 0.3 mg of each compound were percolated through separate foam columns at a flow rate of 5–10 cm^3·min^{-1}. More or less complete retention of the compounds tested was achieved in the foam column. After squeezing

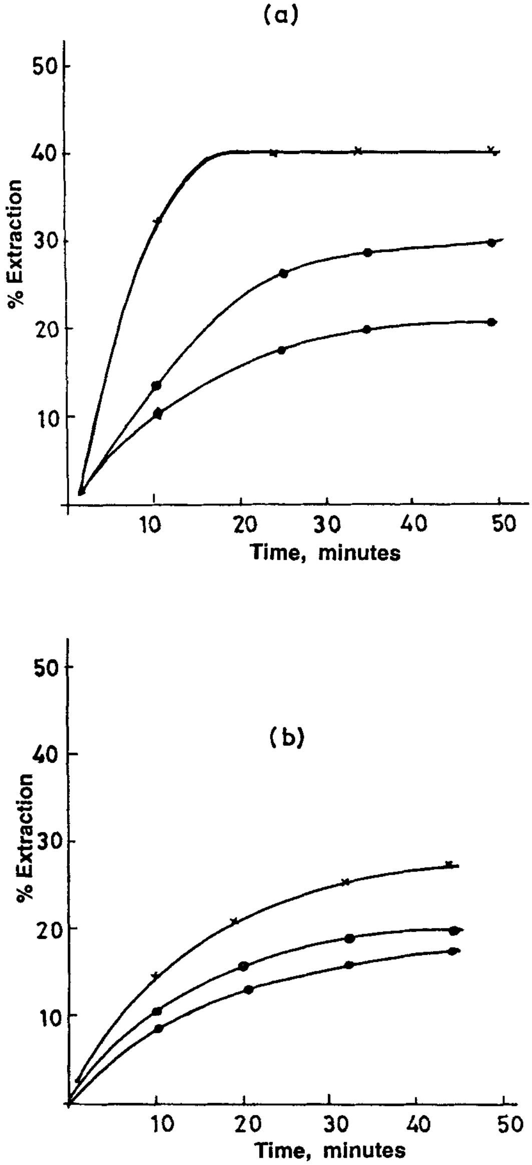

FIG. 4 Effect of ethanol percentage on the extraction of resorcinol (a) and phenol (b): (×) 0%, (○) 5%, (●) 10% ethanol.

water from the foam column, the compounds were then recovered from the foam column with 100 cm^3 acetone in a Soxhlet extractor and determined spectrophotometrically at the maximum absorption wavelength for each species after being concentrated to 25 cm^3. The percentage recoveries of the tested compounds from the aqueous media using the proposed foam column are summarized in Table 1. The dependence of retention of the compounds tested on the flow rate and volume of sample was examined by percolating resorcinol (0.2 mg) through the column at various flow rates and sample volumes. Complete retention of the compound was obtained up to 10 $cm^3 \cdot min^{-1}$ and 3 dm^3 aqueous solution. The extraction efficiency decreased significantly to 70% at 15 $cm^3 \cdot min^{-1}$. The quantitative retention and elution of resorcinol (0.050 mg) were carried out, and the height equivalent to a theoretical plate (HETP) was obtained from the elution curves by using the equation (23):

$$N = \left(\frac{8V_{\max}^2}{w^2}\right) = \left(\frac{L}{\text{HETP}}\right)$$

where N is the number of plates, $V_{\max}$ is the volume of eluate at peak maximum, w is the width of the peak at $1/e$ (the maximum solute concentration), and L is the length of the foam bed. The HETP values were 1.8 and 2.05 mm at flow rates of 2–5 and 10 $cm^3 \cdot min^{-1}$, respectively. The HETP value was also calculated for resorcinal from the breakthrough capacity curve at 10 $cm^3 \cdot min^{-1}$ by using the equation (12):

$$N = \left(\frac{VV'}{(V - V')^2}\right) = \frac{L}{\text{HETP}}$$

where V is the volume of effluent at the center of the S-shaped breakthrough curve where the concentration is one-half the initial concentration, and V' is the volume at which the effluent has a concentration of 0.1578 of the initial concentration. The value of HETP obtained by this method was 1.9 mm, confirming the values obtained from the elution curves. The method has been tested for the separation of *o*-nitrophenol and resorcinol. *o*-Nitrophenol was first eluted with 0.05 M NaOH and resorcinol was then recovered with acetone at a flow rate of 2 $cm^3 \cdot min^{-1}$.

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