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Removal of organic pollutants from aqueous solution

V. Comparative study of the extraction, recovery and chromatographic separation of some organic insecticides using unloaded polyurethane foam columns

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ABSTRACT

The concentration of dissolved insecticides in aqueous media was determined by chromatographic separation on polyurethane foam columns. The results of preliminary screening tests on the removal of insecticides by the unloaded polyurethane foam indicated that a reasonable percentage of the insecticides was retained on the foam. Therefore attempts were made to extract these compounds from aqueous media using foam columns. Various parameters affecting the retention and separation of these compounds were studied, including temperature, flow-rate, pH, insecticide concentration, shaking time, sample volume and eluting solvent. The complete separation and quantitative recovery of these compounds from the foam with acetone in a Soxhlet extractor were achieved. The method can be used to preconcentrate insecticides in tap water and modified to determine dissolved insecticides in industrial and natural waters. Polyurethane foam has a good capacity for use when large volume samples need to be handled and is an inexpensive sorbent compared to other known solid sorbents.

INTRODUCTION

Insecticides can enter water systems from various sources. Edward [1,2] has reported sources of insecticides to include run-off from agricultural land, direct entry from crop spraying, industrial and sewage effluent, cattle spraying, dust and rainfall. The presence of insecticides in the aquatic environment has been known to cause severe health problems to animals, birds and humans [3]. The removal or reduction of these organic pollutants to an acceptable concentration by extraction with steam distillation, solvent extraction, oxidation, or adsorption on carbon or other solid supports has been investigated [4–7]. Such preconcentration techniques are often slow or cumbersome and too expensive for routine use where many large volume samples are concentrated on-site prior to quantitative analysis [7].

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Polyurethane foam has recently been used as an inexpensive solid extractor and effective sorbent for the removal of water pollutants [8–13]. The solid foam concentrates various species in solution by a phase distribution mechanism rather than by adsorption [12,13].

This paper reports the effect of various parameters on the extraction of some organic insecticides from aqueous solution by polyurethane foam and attempts to establish the mechanism of extraction by the unloaded foam.

EXPERIMENTAL

Reagents and materials

All chemicals used were of analytical-reagent grade. Polyurethane foam, an open cell polyether (bulk density 30 kg m^{-3}) was supplied by K.G., Schaum (Stoffwerk, Kremsmunster, Austria). The foam was cut and washed as previously described [9]. Foam loaded with tributyl phosphate (TBP) was prepared by mixing the dried foam cubes with 5% TBP in benzene (5 cm^3 g^{-1} dry foam) with stirring for 10 min. The reagent foams were then dried [9].

The insecticides studied were: Dimethoate, O,O-dimethyl-SCN (methyl carbamoyl methyl) phosphorodithioate (I); Azodrine (Nuvacron), 3-hydroxy-*N*-methyl-*cis*-crotonamide dimethyl phosphate (II); and Lannate (methomyl), 5-methyl-*N*-(methyl carbamoyl) oxythioacetamide (III). Stock solutions (100 μg cm^{-3}) of each compound were prepared in a 100-cm^3 measuring flask by dissolving the exact weight of the insecticide in 5 cm^3 of acetone and diluting with distilled water. A series of standard solutions of these compounds was prepared by diluting their stock solutions with water; the solutions were stored in polyethylene bottles.

Apparatus

A Varian 634 S double-beam UV–visible spectrophotometer with 1-cm quartz cells 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 shaked for various time intervals up to 30 min. 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 then calculated by difference. Following these procedures, the effect of pH, extraction media and temperature were determined. An extraction isotherm was determined for each compound (20–100 μg cm^{-3}).

Flow experiments. In the flow experiments, 1 g of dry foam was packed into the column using the vacuum method of foam column packing [14]. Tap or distilled water (0.5–3 dm^3) samples containing 0.3 mg of each compound were passed through the foam column at 5–10 cm^3 min^{-1}. All the compounds were retained quantitatively. After squeezing water from the foam, the compound was then recovered from the foam

in a Soxhlet extractor with 50 cm^3 of acetone. The analyte was determined by measuring the absorbance of the solution.

The mixture containing Dimethoate (0.1 mg) and Lannate (0.1 mg) was passed through the foam column at 2–3 cm^3 min^{-1}. Dimethoate was washed out first with 100 cm^3 of acetone and Lannate was then recovered with 50 cm^3 of 0.3 *M* sodium chloride at pH 5.

RESULTS AND DISCUSSION

Preliminary experiments have shown that th extraction of the investigated compounds (I, II and III, Fig. 1) by the unloaded and the TBP-loaded polyurethane foam using batch experiments is rapid and equilibrium is reached in less than 30 min, followed by a plateau. The results obtained are summarized in Fig. 2. A better percentage extraction was obtained with the TBP-loaded foam and a shaking time of 30 min was used in subsequent work.

Extraction isotherm

The uptake of the investigated insecticides from aqueous solution by the unloaded and TBP-loaded foam was dependent on their initial concentrations. Therefore, the extraction isotherms were determined over a wide range of equilibrium concentrations (20–100 μg cm^{-3}) for each compound. The results are presented in Fig. 3. The extraction isotherms of the insecticides tested exhibited a first-order behaviour at low concentrations. The adsorption of the different species by the unloaded foam increases in the order: Azodrine > Dimethoate > Lannate. Similar trends were obtained with the TBP-loaded foams. Solvent extraction is therefore the most probable mechanism for the adsorption of these compounds by the unloaded foams. The acidity of the absorbate (pK_a) and the molecular weight obviously play an important role in determining the adsorption efficiency in the TBP-loaded foam; this is also the case with the unloaded foam. The effect of temperature on the extraction efficiency of the unloaded foam was determined at 35 and 45°C. The percentage adsorption increases slightly with increasing temperature.

The effect of pH on the total insecticide removal was carried out over the pH range 3–9. The adsorption profiles of the investigated compounds are given in Fig. 4. It can be seen that the extraction of compounds I and II increases with increasing pH and reaches a plateau at about pH 6. In contrast, compound III displays a minimum removal at pH 5 by the unloaded foam and the percentage removal increases markedly at higher pH.

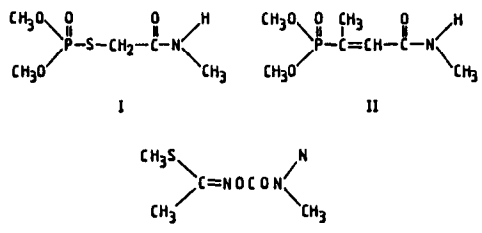

Fig. 1. Structures of I, II and III.

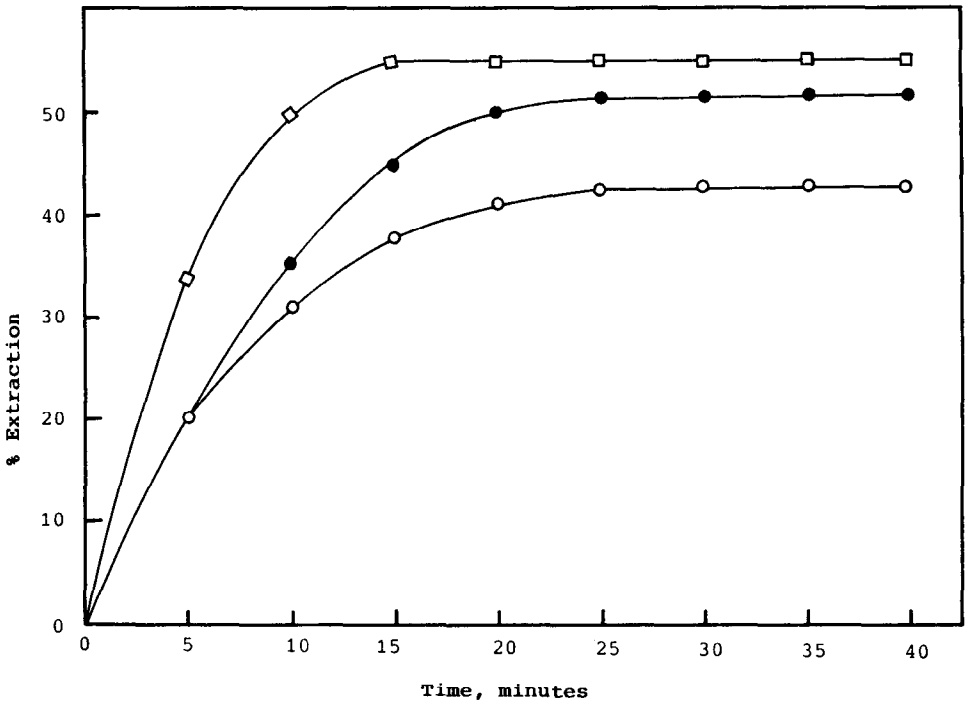

Fig. 2. Effect of shaking time on the extraction of the insecticides by unloaded foam. (□) Azodrine; (●) Dimethoate; and (○) Lannate.

The efficiency and rate of extraction of Lannate by the unloaded foam was generally decreased by the addition of ethanol (0–10%) to the aqueous solution. This is probably due to the formation of inactive species (liophilic association) which are not adsorbed from the aqueous solution [15]. The results are summarized in Fig. 5. The amount of Lannate adsorbed at equilibrium for each ethanol concentration is in the order 0% > 5% > 10% ethanol content. This order agrees with the suggestion of Kirkwood [16] that the smaller the dielectric constant, the larger the amount extracted. Thus, the nature of the media has a marked effect on the adsorption characteristics.

Dynamic experiments

On the basis of the batch experiments, the quantitative retention and recovery of these compounds were investigated using the foam column mode. Distilled or tap water samples (0.5–3 dm^3) containing 0.3 mg of each compound were percolated through separate foam columns at a flow-rate of 5–10 $cm^3\ min^{-1}$. Complete retention of the compounds was achieved. The insecticides were then recovered from the foam columns with 50 cm^3 of acetone in a Soxhlet extractor and determined spectrophotometrically at the maximum absorption wavelength for each species. The results are summarized in Table I. The dependence of recovery on flow-rate through the foam column was investigated by percolating Lannate (0.1 mg) through the column at

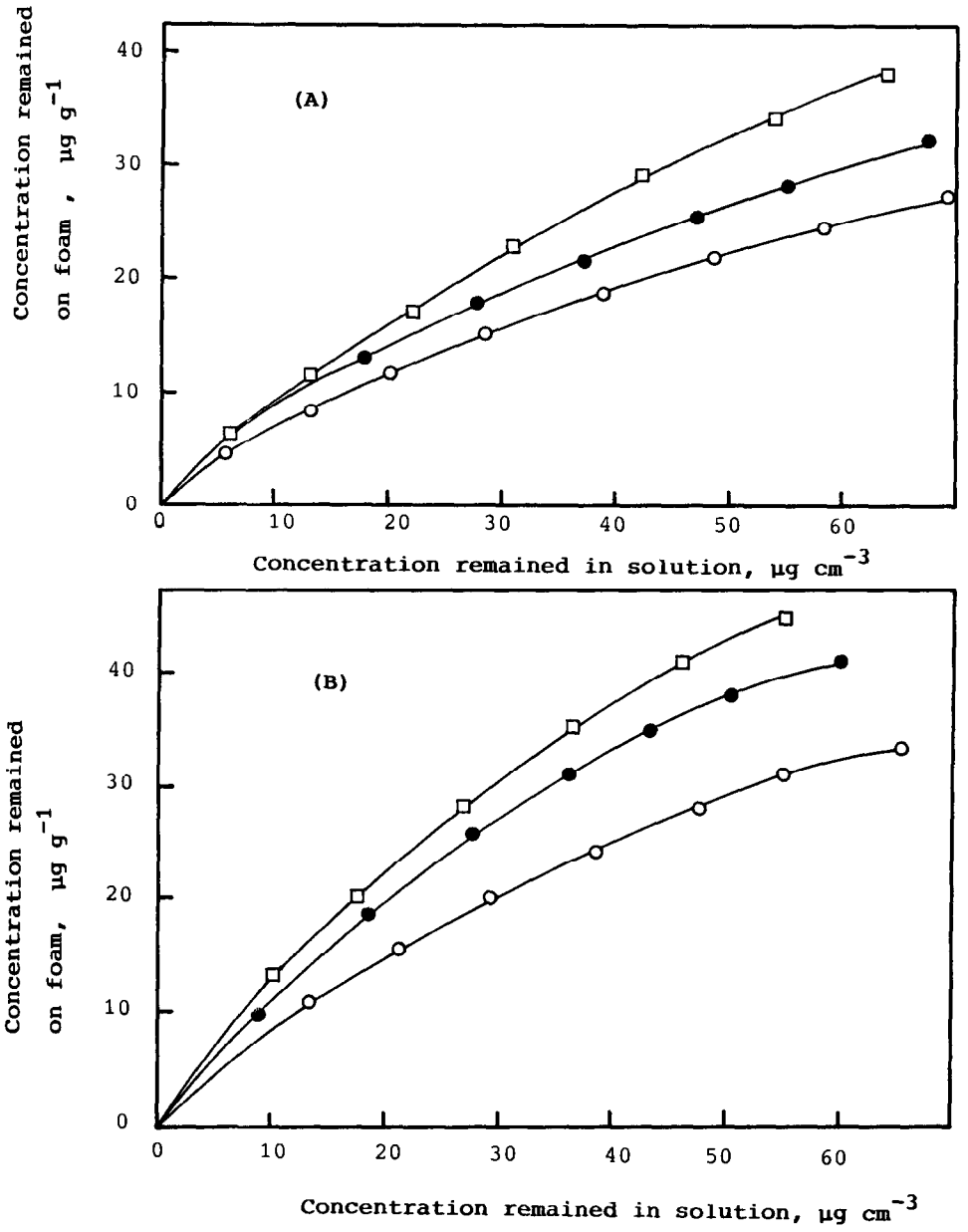

Fig. 3. Extraction isotherms of the insecticides with (A) unloaded foam and (B) TBP-loaded foam. (□) Azodrine; (●) Dimethoate; and (○) Lannate.

various flow-rates. Complete retention of Lannate was obtained up to 10 cm^3 min^{-1} and the efficiency of extraction decreased significantly to 64% at 15 cm^3 min^{-1}.

The quantitative retention and elution of Dimethoate was determined. Fig. 6 shows the chromatograms for eluting Dimethoate at flow-rates of 1–3, 5 and 8–10 cm^3

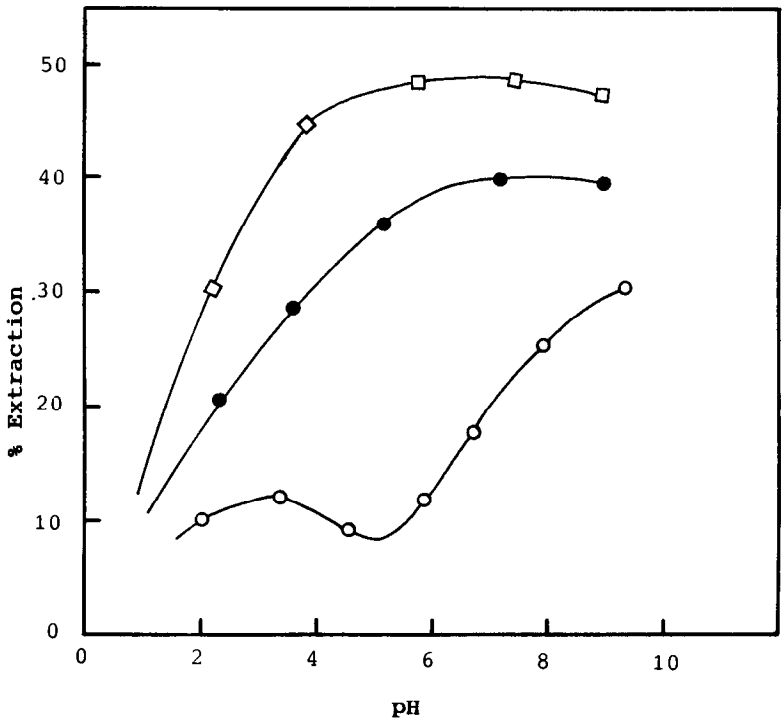

Fig. 4. Effect of pH on the extraction of the insecticides tested with unloaded foam. (□) Azodrine; (●) Dimethoate; and (○) Lannate.

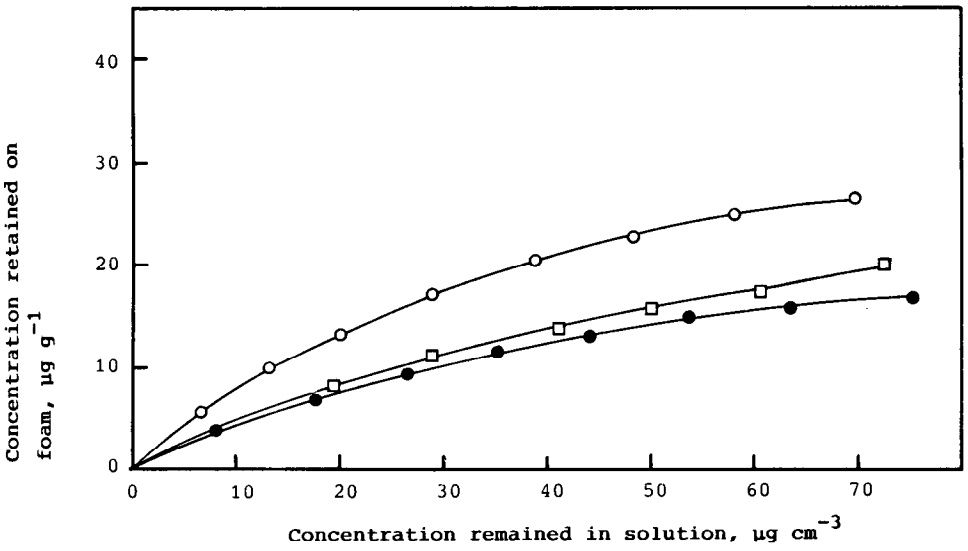

Fig. 5. Effect of ethanol percentage on the extraction of Lannate. (○) 0%; (□) 5%; and (●) 10% ethanol.

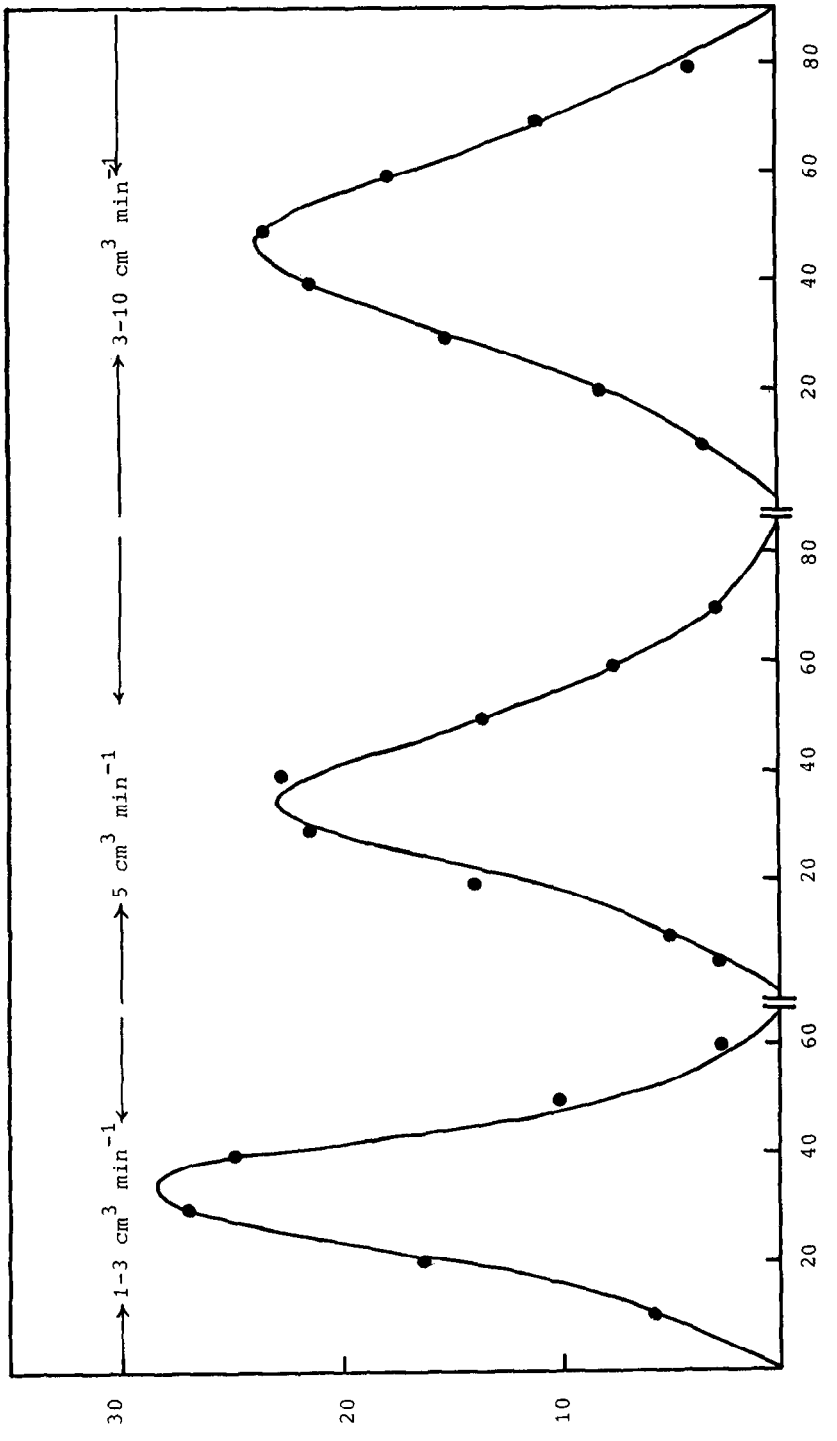

Fig. 6. Effect of flow-rate on the elution of Dimethoate (0.1 mg) with acetone.

TABLE I

EXTRACTION AND RECOVERY OF THE INSECTICIDES

A 0.3-mg mass was extracted from 2 dm^3 of aqueous solution by the unloaded foam columns at 3–5 cm^3 min^{-1}. (a) Average of duplicate determinations from distilled water; (b) average of duplicate determinations from tap water.

Insecticide	Recovery (%)		Wavelength (nm)
	a	b	
Dimethoate	97	94	320
Azodrine	95	98	306
Lannate	93	90	570

min^{-1}. The height equivalent to a theoretical plate (HETP) was calculated from the elution curves using the equation [17]

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

where N = number of plates, V_{max} = volume of eluate at peak maximum, W = width of the peak at 1/e the maximum solute concentration and L = length of the foam bed. The HETP values were 2.1, 2.4 and 2.6 mm at flow-rates of 1–3, 5 and 8–10 cm^3 min^{-1}, respectively. The value of HETP was also calculated from the break-through capacity curve using the equation [11]

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

where $\bar{V}$ is the volume of effluent at the centre of the S-shaped break-through 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 2.3 mm, confirming the values obtained from the elution curves. The proposed column method has been tested for the separation of Dimethoate and Lannate. Dimethoate was eluted first with acetone and Lannate was then recovered with 0.3 M sodium chloride at pH 5 at a flow-rate of 1–2 cm^3 min^{-1}.

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