Retention and Separation Behavior of Some Organophosphorus and Pyrethroid Insecticides on Polyurethane Foams

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The application of polyurethane foam for the preconcentration of Cypermethrin, Malathion and Parathion insecticides was examined by the static mode of extraction. The retention of the tested species from aqueous media with the polyether polyurethane foam suggests that the solvent extraction and the cation chelation mechanism might be operative. Quantitative retention and recovery of the tested insecticides by the foam column mode of separation were carried out and satisfactory recovery percentages (up to $99.10 \pm 3.12\%$) were obtained. The number and the height equivalent of the theoretical plate of the foam columns were found in the range of $165 - 170 \pm 4$ and $1.85 - 1.93 \pm 0.26$ mm, respectively at $10 \text{ cm}^3/\text{min}$ flow rate. Separation of the binary mixtures of Malathion–Cypermethrin and Parathion–Cypermethrin insecticides from the aqueous media was achieved successfully. The helical structure of the foam sorbents offers rapid, versatile and effective separations and preconcentration of different compounds from fluid samples over conventional bulk-type granular sorbents.

Keywords Polyurethane foam, organophosphorous insecticide, pyrethroid insecticide, Parathion, Malathion

As a consequence of the activities of modern industries and agriculture many man-made pollutants have found their way into the environment, without the availability of much knowledge on their possible harmful effect on the environment.^{1,2} The insecticides can enter water systems from agriculture land, direct entry from crop spraying, industrial and sewage effluent, dust and rain fall. The presence of these compounds in the aquatic environment has been known to cause severe health problems to animals and humans.³

The most common reported extraction procedures for the removal or reduction of these pollutants are limited and are too expensive for routine analysis where many large volume samples are concentrated on site prior to quantitative analysis.⁴⁻⁹ The classical paper of Bowen¹⁰ and the pioneering studies of Braun and Farag^{11,12} on the application of polyurethane foam (PuF) sorbents to trace elements led to revealing the potentialities of their geometrical form: spherical membrane-shaped geometry in extraction chromatography.¹⁰⁻²² In this paper, the extraction of some insecticides by polyether based polyurethane foam from large volume water samples is reported. The influence of various parameters on the retention of the tested species was carried out to determine whether the sorption on the polyurethane

foams takes place by solvent extraction mechanism or by other mechanisms.

Experimental

Reagents and materials

All of the chemicals used were of analytical reagent grade. Open-cell polyether based polyurethane foam was supplied by Greiner K. G. Schaum (Stoffwerk, Kremsmunster, Austria). Foam cubes of approximately 1 cm^3 were cut from a polyurethane foam sheet. The foam cubes were washed with HCl (10%v/v) and distilled water. The acid-free foam cubes were then washed with acetone in a Soxhlet extractor for 6 h and dried in an oven at 80°C for 2 h.¹¹ Stock solutions (1 M) of lithium, sodium, ammonium and potassium chlorides were prepared in distilled water. A Britton–Robinson buffer (pH 2–11) was used. The compounds tested were Parathion, *o,o*-diethyl-4-nitrophenyl phosphorothioate; Cypermethrin, cyano(3-phenoxyphenyl)methyl 3-(2,2-dichloroethyl)-2,2-dimethylcyclopropanecarboxylate and Malathion, diethyl[(dimethoxyphosphinothionyl)thio]butanedioate. A stock solution of each compound ($200 \mu\text{g}/\text{cm}^3$) was prepared in a 100 cm^3 measuring flask by dissolving the exact weight of the compound in ethanol. Standard solutions of these compounds were then prepared by diluting their stock solutions with distilled (or tap) water in the presence of few cm^3 of

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ethanol whenever required. The pyrethroid Cypermethrin is extremely lipophilic and adsorbs strongly to glassware; therefore, a freshly prepared stock solution and diluted solutions were prepared directly before the experiment.

Apparatus

A Pye Unicam SP8-100 spectrophotometer was used for recording the absorption spectra and for routine absorbance measurements, with matched 2 mm and 10 mm quartz cells. An Orion pH meter and glass columns (12 cm height $\times$ 10 mm i.d.) and Lab-Line Orbit Environ-Shaker Model 35271-I were also used.

General procedure

Batch experiments. To examine the effect of the shaking time on the uptake of the tested compounds by the polyurethane foam, the foam cubes (0.3 ± 0.004 g) were equilibrated with a freshly prepared 100 cm³ aqueous solution at pH 5–6 of each compound at 80 μ g/cm³ in ethanol–water (5%v/v) in 250 cm³ conical flasks and shaken in a thermostated shaker at $20 \pm 0.1^\circ\text{C}$ for various time intervals of up to 1 h. The aqueous phase was then separated and the amount of the compound remaining in it was determined from absorbance measurements at suitable wavelength against a reagent blank. The insecticide retained on the foam was calculated by the difference of absorbance. Following these procedures, the influence of the compound concentration (10–100 μ g/cm³), solution pH, temperature, ethanol/concentration and increasing salt concentration (≤ 0.1 M) of the different metal (Li, Na, K) chlorides and NH₄Cl on the extraction efficiency of the tested species by the polyurethane foam was determined. The %extraction (E) and the distribution coefficient (D) were calculated employing the equations:

$$\% \text{Extraction} = \left(\frac{A_0 - A}{A_0} \right) \times 100, \quad (1)$$

$$D = \frac{\% \text{Extraction}}{100 - \% \text{Extraction}} \times \frac{\text{Volume of solution (cm}^3\text{)}}{\text{Weight of dry foam (g)}}. \quad (2)$$

Here, A_0 and A are the concentrations of the tested compounds in aqueous solutions before and after extraction, respectively.

Column experiments. One gram of the dry foam was packed into a column using the vacuum method of foam packing.^{11,12} A tap or distilled water (0.1–6 dm³) sample containing 0.01 mg of the compound tested at pH 5–7 was passed through the foam column at 10 cm³/min flow rate. After squeezing water from the foam material, the compound was then recovered from the foam with 100 cm³ acetone in a Soxhlet extractor for 1 h. The sample quantity was then determined by measuring the absorbance of the solution against a reagent blank after being concentrated to 25 cm³ with a rotary evaporator.

The effect of the sample volume and flow rate on the extraction efficiency of the compounds by the foam were also determined.

Results and Discussion

Batch experiments

Batch experiments using polyurethane foams have shown that the retention of the investigated insecticides (Parathion (I); Malathion (II) and Cypermethrin (III)) (Fig. 1) from an aqueous solution at $5 < \text{pH} < 7$ was rapid, and equilibrium was reached in less than 50 min followed by a plateau (Fig. 2; each point in the figure represents the mathematical average of five measurements). Hence, a minimum shaking time of 1 h was adopted in the subsequent work. The average values of the half-life time ($t_{1/2}$) of the equilibrium sorption of the tested compounds on the unloaded foams were found in the range of 3–5 min for Malathion and Cypermethrin and 2–2.5 min for Parathion. These results can be attributed to the high mobilities and diffusion rate of Parathion through the quasi-spherical membrane structure of the foams.

The sorption of the tested insecticides (I, II and III) from the aqueous solution by the polyurethane foam was found to depend on their concentrations. Thus, the sorption isotherms of the tested compounds on the PuF were developed over a wide range of equilibrium concentrations (10–100 μ g/cm³) for each species at 20°C . The pH values of the aqueous solution were adjusted to pH 5–7. The sorption isotherm of the tested insecticides exhibited a first-order behavior in the low-concentration range and tended to a plateau at high bulk-solution concentration. The sorption profiles of the different species (Fig. 3) increased in the order

Similar results were also obtained in diethylether. Thus, a solvent-extraction mechanism might be involved in the sorption of the tested species by the polyether foam.¹⁶ These results do not agree with the general understanding that the larger is the molecular weight (MW) of the absorbate Parathion (MW=291.0), Malathion (MW=362), and Cypermethrin (MW=416) the larger is the amount retained on the foams when the substances concerned are similar in nature.²³ However, the complex nature of the membrane of the polyether foam implies that several mechanisms could be involved simultaneously.^{17–21}

The influence of the pH on the excitation of the tested compounds (80 μ g/cm³) by the foams was examined over the pH range 2–11. Sorption profiles of the compounds by the foams are given in Fig. 4. The percentage removal of the compounds by the foams increased markedly in the pH range 5–7. Lowering the pH (< 4) tends to protonate the nitrogen atoms of the urethane linkage and/or the ether oxygen atoms of the polyurethane foam as follows:¹⁶

Fig. 1 Structures of the organophosphorus insecticides Parathion (I), Malathion (II) and the pyrethroid Cypermethrin (III).

Fig. 2 Effect of the shaking time on the sorption profiles of the tested insecticides (I, II, III) at $80 \mu\text{g}/\text{cm}^3$ in aqueous solution (100 cm^3) at pH 5–7 and $20 \pm 0.1^\circ\text{C}$ by the polyether foams ($0.30 \pm 0.01 \text{ g}$).

or

Thus, sorption of the compounds decreased. On the other hand, the insecticides uptake was also reduced at elevated pH (>7). This is possibly attributed to the increased polarity of the tested species. These data clearly show that the pH values significantly influence the sorption of the tested species.

Fig. 3 Extraction isotherm of Parathion (I), Malathion (II) and Cypermethrin (III) at a concentration of $10 - 100 \mu\text{g}/\text{cm}^3$ by foams ($0.30 \pm 0.01 \text{ g}$) from a 100 cm^3 aqueous solution sample at pH 5–7 and $20 \pm 0.1^\circ\text{C}$ and 1 h extraction time.

Fig. 4 Effect of the pH on the extraction percentage of Parathion (I), Malathion (II) and Cypermethrin (III) at $80 \mu\text{g}/\text{cm}^3$ by the foam ($0.30 \pm 0.01 \text{ g}$) from 100 cm^3 aqueous sample. Other conditions as in Fig. 2.

The influence of various concentrations of alkali metal (Li, Na, K) chlorides and NH_4Cl at concentrations $\leq 0.1 \text{ M}$ on the sorption percentage of the tested compounds at $80 \mu\text{g}/\text{cm}^3$ by the polyether foam was studied at pH 5–7; the results are summarized in Table 1. Significant increases in the distribution ratios of Malathion and Parathion were observed with increasing concentrations from 0.01 to 0.1 M and the following orders of extraction were achieved:

Table 1 The logarithm distribution coefficient (D) data for the sorption of the tested insecticides by the polyurethane foams in the presence of different univalent cations

Cation/M		Logarithm distribution coefficient, D		
		Parathion	Cypermethrin	Malathion
Li ⁺	0.01	3.52±0.16	2.38±0.12	2.42±0.12
	0.05	3.46±0.12	2.52±0.17	2.58±0.12
	0.10	3.42±0.10	32.42±0.12	3.05±0.16
Na ⁺	0.01	3.42±0.13	2.82±0.16	2.28±0.10
	0.05	3.41±0.13	2.39±0.16	2.55±0.12
	0.10	3.40±0.12	2.50±0.17	2.68±0.18
K ⁺	0.01	3.39±0.10	3.75±0.08	2.05±0.14
	0.05	3.36±0.16	3.49±0.19	1.85±0.15
	0.10	3.2 ±0.20	1.79±0.16	3.62±0.12
NH ₄ ⁺	0.01	3.35±0.16	3.50±0.13	2.15±0.16
	0.05	3.31±0.12	2.61±0.12	1.96±0.15
	0.10	3.22±0.16	2.72±0.14	1.84±0.15

Cations: extraction from aqueous solution (100 cm³) at pH of maximum extractibility of each insecticide (80 µg cm⁻³). Average of five measurements±standard deviation (SD) at room temperature.

The distribution ratio of Malathion increased along with the amount of LiCl and NaCl added from log D =2.42 and 2.28 to 3.05 and 2.68 for Li⁺ and Na⁺ ions at 0.01 and 0.1 M, respectively. This behavior is characteristic of a solvent-extraction mechanism with the salt acting as a salting-out medium and the cation-chelation mechanism is excluded.^{15,16} The added salts increased the sorption profiles of the tested compounds into the polyether foams by reducing the number of water molecules available to solvate the organic compounds, which would therefore be forced out of the solvent phase into the foam. In such a case some amount of free water molecules are preferentially used to solvate the ions.

To confirm the salting out of the added salts on the sorption profiles of Malathion and Parathion by the foams, the extraction of a 200 cm³ ethanolic aqueous solution (5%v/v) of the former species (80 µg/cm³) in (v/v) at pH 2 and pH 6 was investigated after 1 h shaking. The added LiCl (0.1 M) to the aqueous media enhanced the distribution ratio of Malathion in a solution of pH 6 (log D =3.05) than at a lower pH of 1 (log D =1.9). These results confirm that both Malathion and Parathion are highly extractable in the neutral form and the solvent-extraction mechanism is the more predominant mechanism.

The sorption profiles of Cypermethrin by the unloaded foams decreased with increasing the concentration (0.001–0.1 M) of the alkali metal (Li⁺, Na⁺, K⁺) and NH₄⁺ chlorides and the following order of sorption was achieved at 0.1 M salt concentration:

Therefore the ion-dipole interaction of NH₄⁺ with the

oxygen sites of the polyurethane foam might be highly predominant in the sorption of Cypermethrin, and the cation chelation mechanism may be operative in the sorption process by the polyurethane foams.^{18–22}

The influence of the temperature on the sorption profiles of the tested insecticides by the polyether foams were determined at 25, 35, 45 and 55°C. The distribution ratios of the tested compounds increased slightly with increasing temperature. Assuming no precipitation or chelation and that the tested insecticides exist in the neutral form at pH 5–7, the equilibrium constant (K) for the equation

is equivalent to the distribution ratio, D .^{22,24} Employing

$$\ln K = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}, \quad (9)$$

the values of the standard enthalpy change ΔH° and the standard entropy change ΔS° for the sorption of the tested compounds on polyurethane foams were calculated. The ΔS° for Malathion and Parathion were found to be -20 ± 2 and -38 ± 4 J/mol deg., respectively while for Cypermethrin the ΔS° was found to be -16 ± 1.8 J/mol deg. The high molecular weight of Cypermethrin (MW=416.6) may account for its higher value of ΔS° . The observed decrease in the ΔS° of Malathion and Parathion is possibly due to the presence of a P=S group, which could reduce the ion-dipole interaction with the oxygen sites of the polyurethane foam. This would therefore reduce the degrees of freedom of movement of the tested organic compound in the polyurethane foam, as previously reported.^{24,25} The results are consistent with the solvent-extraction mechanism. The ΔH° for the tested compounds were found to be in the range 32 ± 3.92 kJ mol⁻¹. Raising the temperature slightly enhanced the retention of the tested species by the foams. Increasing the temperature may facilitate the partition of the compounds through the urethane linkage and/or ether oxygen atoms of the foams. However, the polymeric nature and/or different functional groups of hetero atoms in the foam may also take a part in the sorption process.

The influence of the total ethanol (5–15%v/v) concentration on the preconcentration of the tested compounds by the foam were examined at pH 5–7. The sorption percentage of Malathion (80 µg/cm³) and Parathion decreased by the addition of ethanol to the aqueous solution. This is probably due to the formation of lipophilic association in an aqueous solution.²⁶ Thus, since the species present in an aqueous solution are well solvated it is difficult for these species to form ion pairs in an aqueous solution. These data are also consistent with the fact that with a pair of low dielectric constant, the degree of extraction should increase along with increasing the polarity of the polar process.^{24,25}

Fig. 5 Effect of the extraction media on the sorption profiles of Cypermethrin by a polyether foam at pH 6–7 and 1 h extraction time: 5% (1), 10% (2) and 15% (3)(v/v) ethanol. Other conditions as in Fig. 2.

Thus the solvent-extraction mechanism is the most probable mechanism for the sorption of Malathion and Parathion. In contrast, the sorption profile of Cypermethrin increased along with the increasing ethanol concentration (Fig. 5). Therefore, the nature of the media has a marked effect on the sorption characteristics of the tested compounds.

Flow experiments

Batch experiments on the sorption behavior of the tested compounds from an aqueous sample solution by the polyether foams suggest the possible application of the foam in a column mode for the preconcentration and recovery of the tested insecticides at the optimum pH of sorption for each insecticides. Tap or distilled water samples (0.1–6 dm³) containing 0.01 mg of each insecticide were percolated separately through the polyurethane foam columns, as describes. More or less complete retention of the investigated compounds was achieved by a foam column at 10 cm³/min. The insecticides were then recovered from the foam column up to 99.10±3.10% with 100 cm³ acetone in a Soxhlet extractor. The recovery percentage of the tested insecticides from by the proposed foam column are summarized in Table 2.

The dependence of the sorption profiles of the tested insecticides by the foam column on flow rate (5–25 cm³/min) and sample volume (0.1–6 dm³) were investigated. Aqueous sample (2 dm³) containing 0.01 mg of Parathion were percolated through the foam column at various flow-rates up to 25 cm³/min. Complete retention of Parathion was obtained at flow rates up to 15 cm³/min and decreased significantly up to 85% at a flow rate of 20–25 cm³/min. No significant decrease in the retention percentage was observed upon increasing

Table 2 Extraction and recovery of the tested compounds separately (0.01 mg) from 3 dm³ distilled (a) and tap (b) water by the proposed unloaded foam column

Compound	% Recovery		Wavelength/nm
	(a)	(b)	
Parathion	95.60±2.12	95.91±1.92	273
Malathion	93.50±2.44	99.10±3.12	206
Cypermethrin	94.22±1.80	95.71±1.71	273

Average±RSD for five measurements.

Fig. 6 Breakthrough capacity curves of the sorption profiles on Parathion at 50 µg/cm³ by the polyether foams at flow rate 10 (1) and 20 (2) cm³/min.

the sample volume from 2 to 6 dm³ at a flow rate of <15 cm³/min.

The foam column performance was calculated from the breakthrough capacity curve of Parathion (50 µg/cm³) at 10 cm³/min flow rate (Fig. 6). The height equivalent to the theoretical plates (HETP) was calculated employing Eq. (10),

$$N = \frac{V_1 \cdot V_2}{(V_1 - V_2)^2} = \frac{L}{[\text{HETP}]}, \quad (10)$$

where L =length of the column foam bed, mm; N =number of the theoretical plates; V_1 =volume (cm³) of the effluent at the center of the S-shaped of the breakthrough curve where the concentration is one half the initial concentration and V_2 is the volume (cm³) at which the effluent has a concentration of 0.1578 of the initial concentration. The value of N and HETP obtained by this method were found in the range 165–170±4 and 1.93±0.22 mm, respectively. The HETP values for Malathion were also calculated from its elution curves with acetone at a 10 and 20 cm³/min flow rate and were found to be 1.85±0.26 mm in agreement with the data obtained from the breakthrough capacity curve.

The proposed foam column method has been successfully employed for the separation of binary mixtures of Malathion-Cypermethrin, and Parathion-Cypermethrin insecticides from different volumes (0.1 – 2 dm³) of the aqueous media. A mixture containing 0.05 mg of Malathion (or Parathion) was separated from 0.01 mg of Cypermethrin at pH 1.5 and 0.1 M lithium chloride employing polyether foam column at a 3–5 cm³/min flow rate. The sorption of Malathion (or Parathion) took place while Cypermethrin was not retained on the foam column and collected quantitatively in the effluent. Malathion (or Parathion) was then recovered from the foam column by 100 cm³ acetone in a Soxhlet extractor as described.

Polyether foam in the batch and column modes can be applied to trapping trace amounts of pyrethroid and phosphorous insecticides from a large sample volume of aqueous media. The sorption profiles of Malathion and Parathion in the presence of alkali metal ions were consistent with the "solvent-extraction mechanism", while the extraction profile of Cypermethrin was indicative of a "cation-chelation mechanism." Studies on the extraction of the tested compounds illustrated the importance of the extraction media and the molecular weight of the sorbate. Open-cell-type resilient polyurethane foams exhibit excellent hydrodynamic properties which permit their utilization in rapid separation in the column mode operations at a relatively high flow rate without any significant impairment of the separation efficiency.

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