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THE EXTRACTION AND RECOVERY OF CHLORINATED INSECTICIDES AND POLYCHLORINATED BIPHENYLS FROM WATER USING POROUS POLYURETHANE FOAMS

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SUMMARY

Porous polyurethane foams were used for the extraction and recovery of chlorinated insecticides and polychlorinated biphenyls (PCBs) from water. One litre of tap water was doped at the ppb* level and elution of the adsorbed compounds was complete with 50 ml of acetone and 100 ml of *n*-hexane.

Quantitative recoveries were obtained for the thirteen insecticides used, at a water flow-rate of 100 ml/min. The recoveries for PCBs were 40–99% at 100 ml/min.

The amount of methylene blue adsorbed from aqueous solution by the foams was correlated with the efficiencies of six foams, of different surface areas and bulk densities, for adsorbing chlorinated insecticides and PCBs from water.

INTRODUCTION

The recent discovery that porous polyurethane foams are able to recover quantitatively organochlorine insecticides[1] and polychlorinated biphenyls (PCBs)[2] from water was a major advancement in the analysis of these compounds. The difficulty in identifying and quantitating the sub-ng/l concentrations of insecticides and PCBs often encountered in water samples necessitates a pre-concentration step.

Rosen and Middleton[3] used a filter of activated carbon to recover insecticides from water while, more recently, Ahling and Jensen[4] coated Chromosorb W with Carbowax 4000 monostearate and *n*-undecane using the material as an adsorbent. Aue *et al.*[5] used support-bonded silicones and Musty and Nickless[6] employed Amberlite XAD-4 for extracting insecticides from water. Although adsorption by activated carbon is very efficient, desorption is much less so and the recovered material is often different from the original material owing to catalytic effects exhibited by the carbon. The other adsorbents all require elaborate treatment or preparation before use and are relatively expensive, whereas porous polyurethane foam only requires a minimum

* Throughout this article the American billion (10^9) is meant.

of preparation, is inexpensive and enables a rapid and efficient extraction to be performed.

This paper compares the ability of six polyurethane foams of different bulk densities and surface areas to recover organochlorine insecticides and PCBs from water both when uncoated and when coated with silicone oil DC-200. A method of determining the potential of a polyurethane foam for recovering these compounds is given followed by an investigation into the effect of water flow-rate, pH of the water and the coating material on the efficiency of the best polyurethane foam. The foam is then applied to the analysis of real water samples.

EXPERIMENTAL

Polyurethane plugs 2.2 cm in diameter and 4 cm long in the case of foam A and 2.2 cm in diameter and 8 cm long in the case of foams B, C, D, E and F were cut from polyurethane foam blocks. These plugs were Soxhlet-extracted with acetone for 24 h and then stood on end on filter papers to dry. The coated plugs were prepared by soaking in a 1% solution of the chromatographic stationary phase in a suitable solvent.

In the case of foam A, two plugs (except where otherwise stated) were placed into a 20 $\times$ 2 cm, I.D. glass column above a sintered glass disc which acted as a base. One plug was used for each of the other foams.

Sufficient acetone was added to cover the plug(s) and a glass rod was used to compress the plug(s) in order to remove any air bubbles. The acetone was washed away with approximately 250 ml of tap water before passage of the doped water through the plugs.

One litre of tap water was doped with the insecticides of interest at the concentrations, and passed through the foam plugs at the flow-rates shown. After sampling, the plugs were squeezed dry and the insecticides eluted with 50 ml of acetone and 100 ml of *n*-hexane. Each experiment was performed in duplicate and the results quoted are an average of the two experiments.

AnalaR quality acetone was distilled in all-glass apparatus before use. The *n*-hexane was purified by distillation after sulphonation of the aromatic impurities. A negligible background was obtained with a fifty-fold concentration of the solvents.

The extracts were concentrated down to 5 ml and injected into a Pye 104 gas chromatograph fitted with a ^{63}Ni electron capture detector operating in the pulse mode and fitted with a 5-ft. glass column of 4 mm I.D. The column was packed with Gas-Chrom Q (100–120 mesh) coated with 1.5% OV-17 + 1.95% QF-1. Argon was the carrier gas at a flow-rate of 50 ml/min. The column temperature was 200° and the detector temperature 300°.

The potential efficiency of a polyurethane foam for recovering insecticides and PCBs from water was determined by measuring the adsorption of the cationic dye, methylene blue from aqueous solution[7,8].

A known weight of foam was left in contact with a methylene blue solution of specific concentration for 24 h. The amount of methylene blue adsorbed onto the foam was determined colorimetrically at 610 nm. This was carried out using each foam over a range of methylene blue concentrations covering 0.001–0.200 mmoles/l. A plot of the amount of methylene blue adsorbed onto the polyurethane (mmoles/kg) *versus* the original concentration of methylene blue (mmoles/l) was made for each foam. A long plateau was obtained at the maximum amount of methylene blue adsorbed onto 1 kg of foam. A typical plot is shown in Fig. 1. This value gives a measure of the potential efficiency of a polyurethane foam for recovering insecticides and PCBs from water.

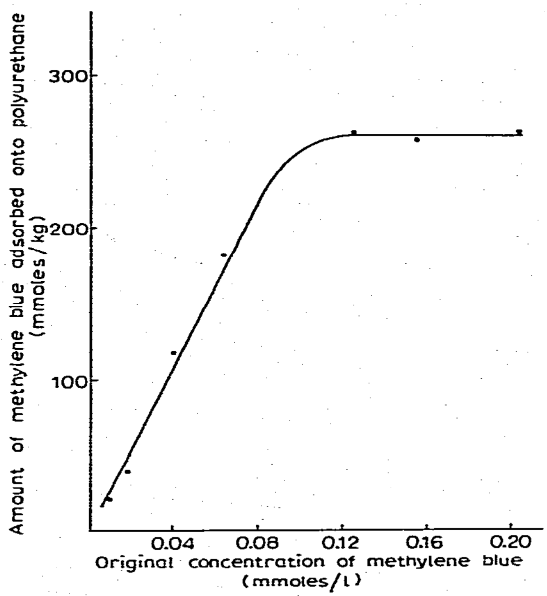

Fig. 1. A typical plot of the amount of methylene blue adsorbed onto polyurethane *versus* the original concentration of methylene blue.

RESULTS AND DISCUSSION

The results given in Table I show the recoveries obtained using six foams of different surface areas and bulk densities, both when uncoated and when coated with DC-200. The results show that in most cases, higher recoveries are obtained when using uncoated foams than when using coated foams. Foam A gives the best recoveries, followed by foam D, followed by foams B, C, E, and F.

The results presented in Table II show the maximum amount of methylene blue adsorbed onto 1 kg of each foam. It can be seen that foam A adsorbs the greatest amount of methylene blue (260 mmoles/kg) followed by foam D (156 mmoles/kg) followed by foams B, C, E and F (96, 70, 28 and 116 mmoles/kg, respectively). These results are in agreement with the recoveries obtained using the six foams and so the determination of the amount of methylene blue adsorbed from aqueous solution should offer a simple and relatively rapid method for determining the potential efficiency of a polyurethane foam for recovering insectides from water. A value in the region of 250 mmoles/kg is adequate and indicates a foam suitable for use as an adsorbent for these compounds.

It must be pointed out, however, that the amount of methylene blue adsorbed by polyurethane foams is extremely dependent on time, possibly owing to a specific

TABLE I

A COMPARISON OF THE RECOVERIES OBTAINED USING SIX FOAMS OF DIFFERENT SURFACE AREAS AND BULK DENSITIES

Water flow-rate, 10 ml/min.

Insecticide	*Concentration (ppb)*	*Foam A*		*Foam B*		*Foam C*		*Foam D*		*Foam E*		*Foam F*	
		Uncoated (%)	*Coated with DC-200 (%)*	*Uncoated (%)*	*Coated with DC-200 (%)*	*Uncoated (%)*	*Coated with DC-200 (%)*	*Uncoated (%)*	*Coated with DC-200 (%)*	*Uncoated (%)*	*Coated with DC-200 (%)*	*Uncoated (%)*	*Coated with DC-200 (%)*
α-BHC	1	101	83	61	46	64	61	65	72	57	52	70	65
Lindane	1	101	77	60	49	64	66	66	70	58	57	68	60
β-BHC	1	101	91	62	48	63	77	77	82	63	66	66	66
Aldrin	1	99	77	50	39	52	46	61	60	61	59	57	51
p,p'-DDE	2	106	81	70	58	96	79	103	103	93	97	83	76
Dieldrin	1	106	88	71	58	85	69	94	96	70	72	78	76
Endrin	10	100	106	69	51	91	88	99	105	91	88	84	76
o,p'-DDT	10	113	106	52	48	75	66	80	88	70	72	64	50
p,p'-DDD	2	102	81	64	57	64	59	82	90	69	68	75	74
p,p'-DDT	10	114	88	47	50	68	61	64	73	69	68	59	44

TABLE II

MAXIMUM AMOUNT OF METHYLENE BLUE ADSORBED

Foam	*Maximum amount of methylene blue adsorbed onto 1 kg of foam (mmoles/kg)*
A	260
B	96
C	70
D	156
E	28
F	116

interaction between the surface of the polyurethane foam and the methylene blue, resulting in the formation of physically adsorbed multilayers.

In order to compensate for this, the time the polyurethane foam is left to equilibrate with the methylene blue solution must be uniform, in this case, 24 h. Shorter or greater times of equilibration would result in lower or higher values respectively.

The results given in Table III show a comparison of the recoveries obtained when the water flow-rate through the most efficient foam, foam A, is varied. Increasing the water flow-rate results in a decrease in recovery, both for the uncoated foam and the DC-200-coated foam. At flow-rates of 10 and 30 ml/min, the uncoated foam is the more efficient, whereas at a flow-rate of 250 ml/min, the coated foam is the more efficient. This would suggest that the foam coated with DC-200 is more efficient than the uncoated foam at adsorbing insecticides from water, but desorption is more difficult.

The results given in Table IV show the effect of different coating materials, *viz.* DC-200, QF-1, SE-30 and DC-11, on the recoveries when using foam A. No

TABLE III

THE EFFECT OF WATER FLOW-RATE ON RECOVERY FOR FOAM A, BOTH WHEN UNCOATED AND WHEN COATED WITH DC-200

Two plugs, 2.2 cm diameter and 4 cm long, were used.

Insecticide	*Concentration (ppb)*	*Recovery (%)*					
		Uncoated			*Coated with DC-200*		
		10 ml/min	*30 ml/min*	*250 ml/min*	*10 ml/min*	*30 ml/min*	*250 ml/min*
αBHC	1	101	95	49	83	86	66
Lindane	1	101	91	40	77	77	61
β-BHC	1	101	86	44	91	83	61
Aldrin	1	99	73	46	77	67	54
p,p′-DDE	2	106	77	68	81	81	77
Dieldrin	1	106	77	58	88	82	76
Endrin	10	100	94	54	106	91	64
o,p′-DDT	10	113	84	43	106	57	56
p,p′-DDD	2	102	89	57	81	80	52
p,p′-DDT	10	114	100	26	88	62	30

TABLE IV

THE EFFECT OF DIFFERENT COATING MATERIALS ON RECOVERY USING FOAM A

Two plugs, 2.2 cm diameter and 4 cm long, were used.

Insecticide	*Concentration (ppb)*	*Recovery (%)*									
		Uncoated		*Coated with DC-200*		*Coated with QF-1*		*Coated with SE-30*		*Coated with DC-11*	
α-BHC	1	101	95	83	86	84	71	80	72	61	58
Lindane	1	101	91	77	77	83	76	81	74	56	52
β-BHC	1	101	86	91	83	87	85	80	79	64	65
Aldrin	1	99	73	77	67	71	57	58	59	65	62
p,p'-DDE	2	106	77	81	81	68	71	66	66	102	95
Dieldrin	1	106	77	88	82	77	74	73	75	105	88
Endrin	10	100	94	106	91	95	76	87	67	73	69
o,p'-DDT	10	113	84	106	57	94	69	84	67	75	65
p,p'-DDD	2	102	89	81	80	73	70	68	73	89	92
p,p'-DDT	10	114	100	88	62	77	72	68	75	59	46

TABLE V

THE RECOVERIES OF PCBs USING FOAM A AT A WATER FLOW-RATE OF 10 ML/MIN

Two plugs, 2.2 cm diameter and 4 cm long were used.

Aroclor	*Concentration (ppb)*	*Recovery (%)*
1242	10	69
1248	10	62
1254	20	75
1260	20	42

TABLE VI

THE EFFECT OF pH OF DOPED WATER ON RECOVERY WHEN USING FOAM A (UNCOATED) WATER FLOW-RATE 10 ML/MIN

Two plugs, 2.2 cm diameter and 4 cm long, were used.

Insecticide	*Concentration (ppb)*	*Recovery (%)*				
		pH 5	*pH 6*	*pH 7*	*pH 8*	*pH 9*
α-BHC	1	75	117	102	101	112
Lindane	1	75	114	103	101	112
β-BHC	1	75	110	103	101	116
Aldrin	1	81	94	96	99	109
p,p'-DDE	2	96	115	119	106	117
Dieldrin	1	97	116	117	106	117
Endrin	10	94	108	107	100	110
o,p'-DDT	10	85	114	108	113	109
p,p'-DDD	2	117	119	119	102	118
p,p'-DDT	10	60	117	96	114	98

coated foam yields a better recovery than the uncoated foam at the flow-rates used. The different coating materials give no marked variations in recoveries.

The results given in Table V show the recoveries of PCBs (Aroclor mixtures) obtained when using foam A while Table VI indicates the effect of the pH of the doped water on the recovery when using foam A. Over the pH range 6–9, the recoveries are generally 100% or above, only at pH 5 do slightly decreased recoveries occur. (The pH of tap water was 8.) The results given in Table VII show the recoveries of heptachlor and Endosulfan I and II when using foam A, quantitative recoveries also being obtained.

TABLE VII

THE RECOVERIES OF HEPTACHLOR AND ENDOSULFAN I AND II, USING FOAM A

Water flow-rate, 10 ml/min. Two plugs, 2.2 cm diameter and 4 cm long, were used.

Insecticide	*Concentration (ppb)*	*Recovery (%)*
Heptachlor	1	99
Endosulfan I	2	101
Endosulfan II	2	100

The results shown in Tables VIII and IX, give the recoveries of insecticides and PCBs at the higher flow-rates when using four plugs of foam A.

At 100 ml/min, the recoveries of insecticides are around 100%, similarly for Aroclors 1242, 1248 and 1254. However, the recovery of Aroclor 1260 at 100 ml/min is only 40%. Decreased recoveries are obtained for both insecticides and PCBs at 250 ml/min.

Finally, in order to demonstrate the applicability of this method to the analysis of a real water sample, 30 l of water, taken from the River Avon at Dauntsey, were

TABLE VIII

RECOVERIES OF INSECTICIDES AT HIGHER FLOW-RATES, USING FOAM A

Four plugs, 2.2 cm diameter and 4 cm long, were used.

Insecticide	*Concentration (ppb)*	*Recovery (%)*	
		Flow-rate 250 ml/min	*Flow-rate 100 ml/min*
α-BHC	1	67	91
Lindane	1	62	91
β-BHC	1	60	100
Aldrin	1	82	93
p,p'-DDE	2	97	106
Dieldrin	1	87	100
Endrin	10	80	108
o,p'-DDT	10	62	103
p,p'-DDD	2	86	102
p,p'-DDT	10	46	109
Heptachlor	1	69	93
Endosulfan I	2	70	95
Endosulfan II	2	65	94

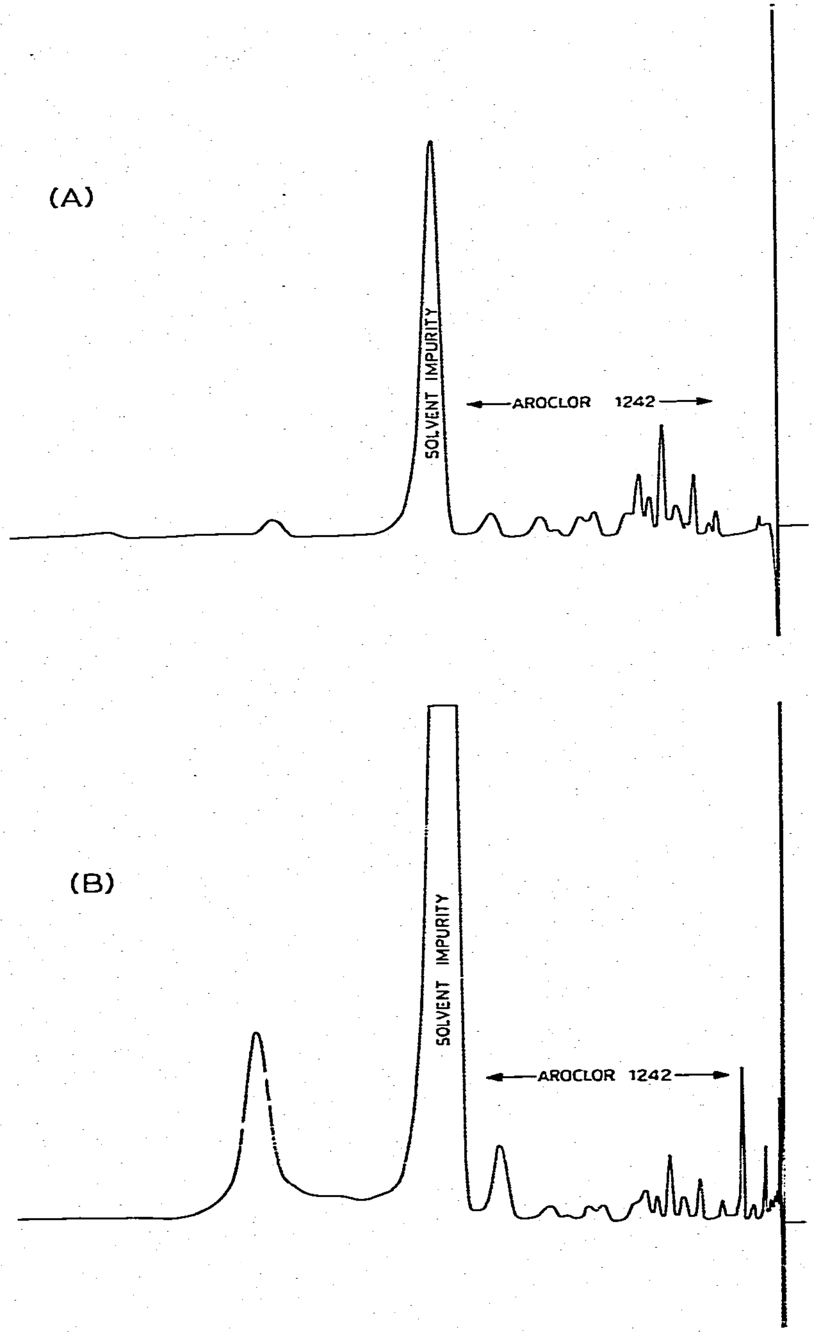
(A)
SOLVENT IMPURITY
AROCLOR 1242
(B)
SOLVENT IMPURITY
AROCLOR 1242

Fig. 2.

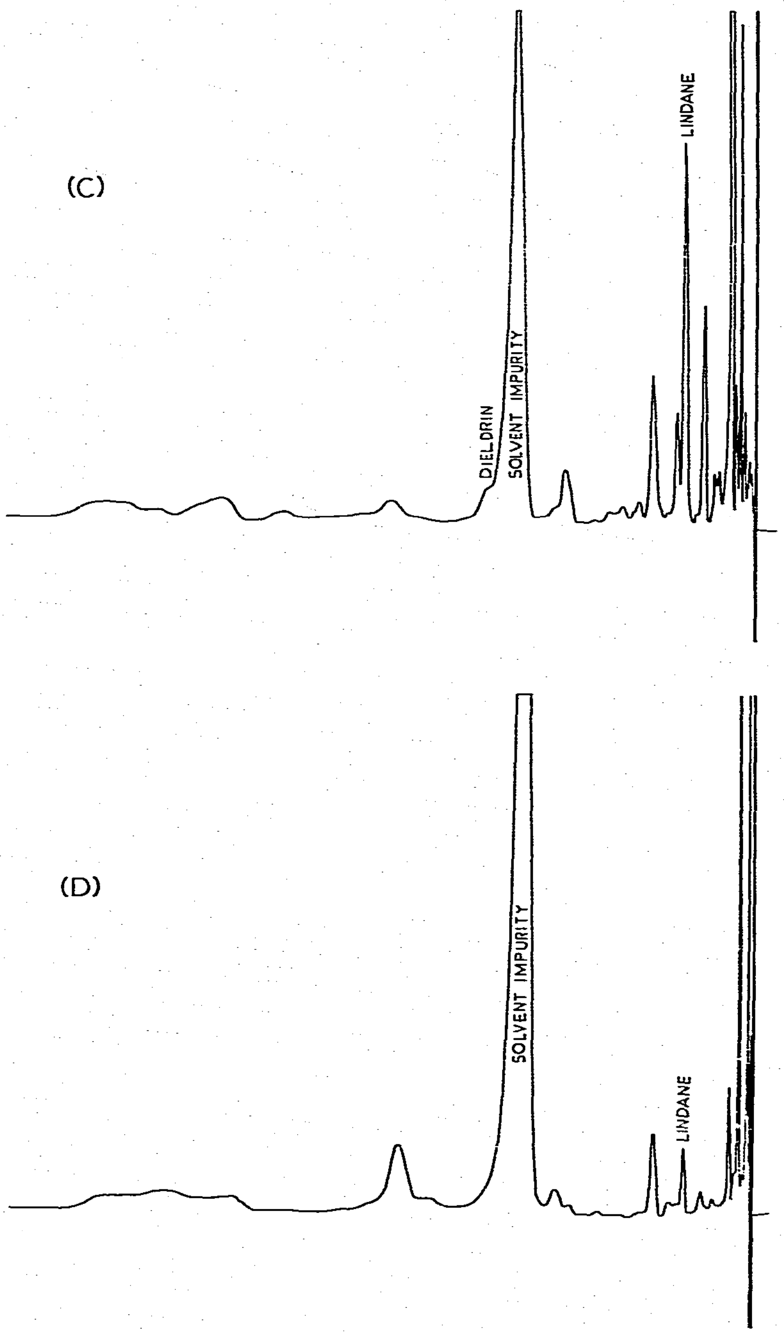

Fig. 2. Chromatograms obtained using 1.5% OV-17 + 1.95% QF-1 on Gas-Chrom Q (100–120) 5-ft. column. Conditions as given previously. (A) *n*-Hexane eluate from the Florisil cleanup of the water. (B) *n*-Hexane eluate from the Florisil cleanup of the sediment. (C) 15% Diethyl ether in *n*-hexane eluate from the Florisil cleanup of the water. (D) 15% Diethyl ether in *n*-hexane eluate from the Florisil cleanup of the sediment.

TABLE IX

RECOVERIES OF PCBs AT HIGHER FLOW-RATES USING FOAM A

Four plugs, 2.2 cm diameter and 4 cm long, were used.

Aroclor	*Concentration (ppb)*	*Recovery (%)*	
		Flow-rate 250 ml/min	*Flow-rate 100 ml/min*
1242	10	74	87
1248	10	78	99
1254	20	76	94
1260	20	29	40

passed through four plugs of foam A at a water flow-rate of 100 ml/min. A wad of pre-extracted glass wool was placed on top of the plugs in order to remove the larger suspended particles. These suspended particles were analysed separately. The time taken for the 30 l of water to pass through the plugs was 5 h.

The polyurethane plugs were eluted with 50 ml of acetone followed by 100 ml of *n*-hexane, and after passage through anhydrous sodium sulphate, the concentrated extract was passed through a column containing 15 g of activated Florisil. Elution was performed with (1) 200 ml of *n*-hexane, and (2) 200 ml of 15% diethyl ether in *n*-hexane.

The sediment was dried at 110° for 3 h and 1 g was extracted with 100 ml of *n*-hexane–acetone (41:59). The subsequent cleanup being the same as for the water sample.

The extracts were analysed by electron capture gas chromatography using two different columns: 1.5% OV-17 + 1.95% QF-1 and 4.75% OV-17.

Fig. 2a shows the chromatogram of the *n*-hexane eluate from the Florisil clean-up of the water and Fig. 2b shows the chromatogram of the same eluate of the sediment. Aroclor 1242 was found to be present in the water at a concentration of 33 ng/l and on the sediment at 750 μg/kg.

Fig. 2c shows the chromatogram of the 15% diethyl ether in *n*-hexane eluate from the Florisil cleanup of the water and Fig. 2d shows the chromatogram of the same eluate of the sediment.

Lindane and dieldrin were found in the water at concentrations of 11 and 2 ng/l, respectively, whilst 60 μg/kg of lindane were found on the sediment.

CONCLUSIONS

(1) A polyurethane foam which adsorbs approximately 250 mmoles/kg of methylene blue in 24 h is suitable for use as an adsorbent for chlorinated insecticides and PCBs.

(2) Higher recoveries are obtained with uncoated foams than with foams coated with chromatographic greases, except at very high flow-rates.

(3) Any pH in the range of 6 to 9 will enable quantitative recoveries to be obtained.

(4) Quantitative recoveries can be obtained for thirteen insecticides at a water flow-rate of 100 ml/min using four uncoated plugs of foam A.

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