Qatar Univ. Sci. J. (1994), 14 (C) : 14-17

SEPARATION AND PRECONCENTRATION OF MALATHION AND AZAMETHIPHOS BY UNLOADED POLYURETHANE FOAMS

By

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فصل وتركيز مبيدات المالثيون والآزاميثفوس بواسطة عديد اليوريثان الرغوي

أحمد محمد الوكيل و عبد الفتاح بسطاوي فرج و عبد الفتاح محمد يوسف
و خالد طولان

دُرست جدوى إستخدام عديد اليوريثان الرغوي غير المحمل لاستخلاص وفصل مبيدات المالثيون والآزاميثفوس بالتقنية الإستاتيكية وتقنية العمود . وقد أختبر تأثير كل من الأس الهيدروجيني والقوة الأيونيه ووقت الرج ووجود بعض المركبات الفلزية في الوسط المائي على خواص إمتصاص المالثيون والآزاميثفوس .

وقد أختبر كذلك تأثير سرعة سريان المحلول على كفاءة فصل هذه المبيدات في النظام الديناميكي . وقد ثبت أن إمتصاص كلا من المالثيون والآزاميثفوس كان كاملا عند إستخدام سرعات سريان تصل إلى ٢٠سم٣/ دقيقة .

وكذلك ثبت نجاح تركيز المبيدات المدروسة وفصلهما بالطريقة المقترحة .

Key Words: Separation, Preconcentration, Malathion, Azamethiphos, Polyurethane foams.

ABSTRACT

The feasibility of using unloaded polyether type polyurethane foams for the extraction and separation of malathion and azamethiphos in batch and column operations has been examined. The effects of pH, ionic strength, shaking time and some metal species present in the aqueous solution on the sorption behaviour of malathion and azamethiphos have been investigated. In dynamic systems, the effect of flow rate on the collection efficiencies of these insecticides has been investigated. The uptake of malathion and azamethiphos on unloaded polyurethane foam columns is quantitative at flow rates up to 20 $cm^3.min^{-1}$. Preconcentration of the insecticides examined and their subsequent separation are successful.

INTRODUCTION

Solid stationary phases are many, among which polyurethane foams are well characterized of being resilient and unique in their hydrodynamic properties[1-2]. This allows the use of new techniques (e.g. pulsating column methods) not suitable with other stationary phases[2] as well as facilitating much higher flow rates.

Polyurethane foam has been recommended as an efficient collector for many pesticides present in low concentrations in aqueous media [3-5]. Utmost care should be paid to minimise or eliminate if possible the great concern for the environment and consequent public hazards.

The growth of the pesticide industry has been spectacular (herbicides, insecticides and fungicides: approximately as 65%, 30%, 5%, respectively). The best known insecticides are the highly chlorinated ones, e.g., DDT, aldrin, dialdrin, chlordane and lindane. The use of organic chlorine compounds as pesticides have been severely restricted in many countries. A second major class of insecticides are the organophosphates, exemplified by malathion and parathion. These substances are less persistent in the environment than the chlorinated hydrocarbons, being hydrolysed and oxidised to noninjurious products fairly rapidly. The third major class of insecticides are the carbamates, of which carbaryl (Sevin) is a good example. Carbamates are widely used because of their low toxicity to higher animals and their rapid rates of disintegration in the biosphere.

The aim of the present study is to explore the wide potentiality of polyurethane foams for extracting many pesticides present as traces in aqueous solutions.

EXPERIMENTAL

Reagents and Materials

All chemicals used were of analytical grade unless otherwise specified. Polyurethane foam of polyether type (bulk density 30 Kg. m^{-3}) was supplied by Greiner, K. G. Schaumstofwerk-Kremsmunster, Austria. Malathion; diethyl (dimethoxythiophosphorylthio) succinate, was obtained from the American Cyanamide Company. Azamethiphos: S-(6-chloro-oxazolo(4,5-bipyridin-2(3H)-on-3-(methyl)O, O-dimethylphosphorothioate. Alfacron was an original sample obtained from Analytica Development AG, Ciba-Geigy Ltd, Basle, Switzerland. These insecticides were used as received. Stock solutions containing 123 and 110 μg. cm^{-3} of malathion and azamethiphos, respectively, were prepared by dissolving the appropriate amounts in distilled water.

Apparatus

Spectrophotometer, Perkin-Elmer (Lambda 38) with one cm matched quartz cells was used. Mechanical shaker, G-10 Gyrotory shaker, New Jersey, USA (0-600 RPM) was used at 450 RPM. Stoppered flasks, 50 ml polyethylene bottles were used in batch sorption experiments. Glass columns of 10 mm diameter and 20 cm length were employed.

Column Preparation

Polyurethane foam (cubes of about 5 mm edge) was washed and dried as previously described[2]. 3 g dry foam cubes were packed in the glass column using the vacuum method of foam column packing[2] to produce 10 cm bed height.

RESULTS AND DISCUSSION

The practical utility of unloaded polyurethane foam for the collection and recovery of the insecticides: malathion and azamethiphos has been examined and the effect of various parameters has been investigated.

Effect of pH: The effect of pH of the aqueous solution on the extractability of malathion and azamethiphos by unloaded polyurethane foam was carried out in batch experiments over the range 2-12 by mixing 0.1 g dry foam cubes with 10 cm^3 aqueous solution containing 492 and 550 μg of malathion and azamethiphos, respectively, in stoppered polyethylene bottles. The flasks were then shaken for 2 hrs and a portion of the aqueous solution is analyzed spectrophotometrically at the specified wavelengths. The amounts of insecticides extracted with the foam were calculated by difference. The extraction profiles of the investigated insecticides are given in Fig. 1. It can be seen that the extraction of malathion increased with increasing pH and reaches plateau in pH 4-5. The extraction of malathion was then decrease at higher pH levels. These results are generally in good agreement with those reported early[6]. On the other hand, azamethiphos show minimum extraction in pH 2-9 and the percentage retention increases markedly at higher pHs. In conclusion, malathion and azamethiphos can be suitably extracted from aqueous solution at pH 4.2 and 11.5, respectively.

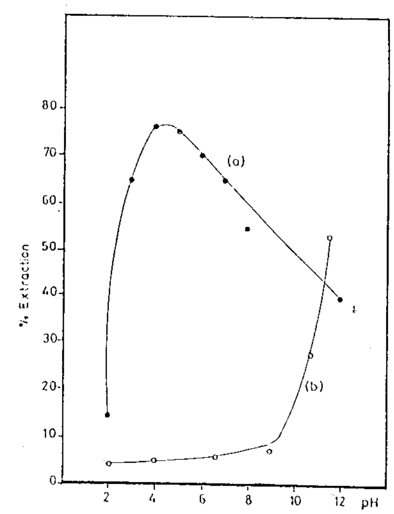

Fig. 1 Effect of pH on the extraction of the insecticides with unloaded polyurethane foam.
(a) Malathion (b) Azamethiphos

Effect of Shaking Time: The rates of extraction of malathion (246 μg) and azamethiphos (770 μg) were investigated in a batch extraction mode by mixing 0.1 g dry foam with 10 cm^3 of aqueous solution, adjusted to the optimum pH for the extraction of each insecticide, in stoppered polyethylene flasks. The flasks were then shaken for different times (1-60 min.). It can be seen from Figs. 2 and 3 that the uptakes of the insecticide examined by the unloaded foam are fast. The half-life times of equilibrium sorption were calculated from Figs. 2 & 3 and found to be 2.0 and 4.0 min. for malathion and azamethiphos, respectively. It is clear from the curves that sorptions of these insecticides take place in one fast step.

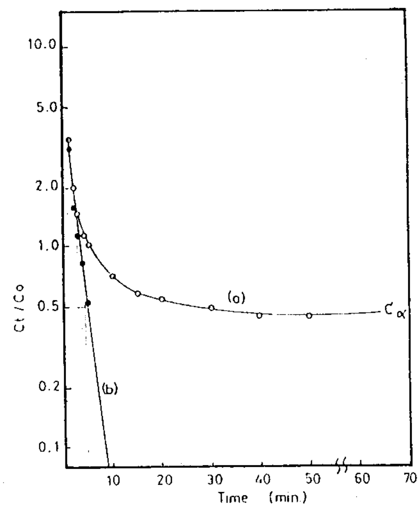

Fig. 2 Rate of sorption of malathion on unloaded foam at room temperature.

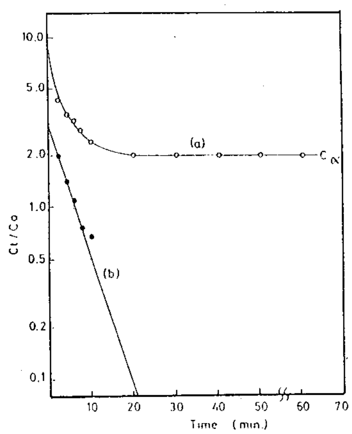

Fig. 3 Rate of sorption of azamethiphos on unloaded foam at room temperature.

Extraction Isotherms : The uptake of the insecticides tested by the unloaded polyurethane foam was found to depend on the concentration of the insecticides in the aqueous solution. Generally, the isotherms show good linear relationships over relatively wide range of insecticide concentration. Fig. 4 shows, for example, the sorption isotherm of azamethiphos by polyurethane foam.

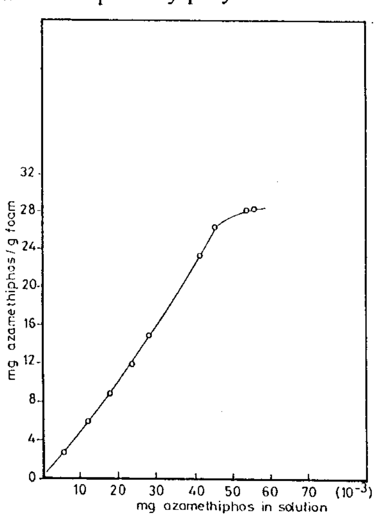

Fig. 4 Extraction isotherm of azamethiphos by unloaded foam.

Effect of Ionic Strength : The effect of ionic strength on the extraction of malathion and azamethiphos was examined by using different electrolytes (NaCl, KCl and NH_4Cl) in concentration range 0.005-0.25 M. The effect of such electrolytes on the extraction of malathion on the foam is clearly pronounced and the extraction increases in the order: NaCl > KCl > NH_4Cl. However, this effect is much lesser in the case of azamethiphos, but show the same order and is almost negligible in the presence of NH_4Cl. (Fig 6).

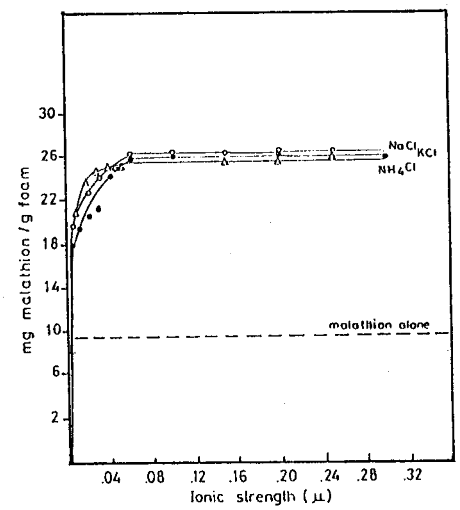

Fig. 5 Effect of different electrolytes on the extraction isotherms of malathian on unloaded foam.

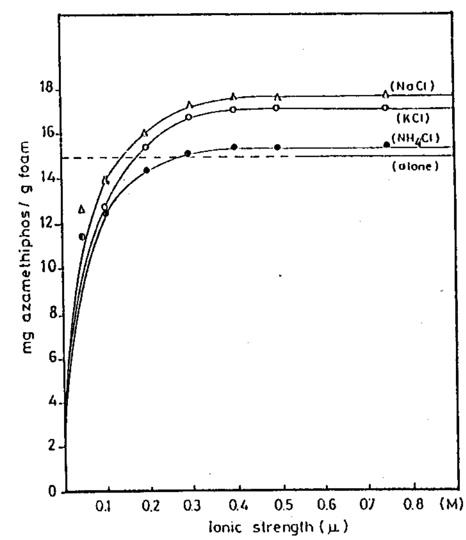

Fig. 6 Effect of different electrolytes on the extraction isotherms of azamethiphos on unloaded foam.

Worthmentioning is that the extraction of the tested insecticides is increased remarkably in the presence of cadmium nitrate or cadmium sulphide in the aqueous solution. This effect is much more clear in the case of malathion (Fig. 7). That is, the presence of some metal ions, which is common in most polluted areas may favour the collection of organic insecticide on the unloaded polyurethane foam. It is worth to note that cadmium sulphide is firmly retained on the surface of the unloaded polyurethane foam cubes.

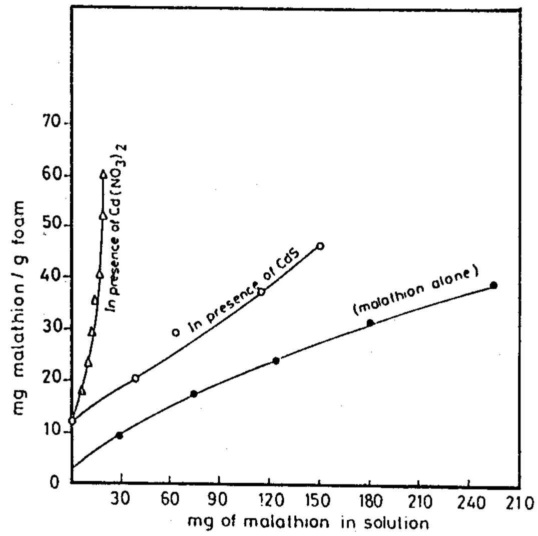

Fig. 7 Effect of metal ions on the extraction isotherms of malathion by unloaded foam.

Dynamic Experiments: On the basis of the batch experiments, the quantitative retention and recovery of these insecticides were investigated using the foam column extraction mode. When 1.23 mg of malathion (10 cm^3) in aqueous solution adjusted to pH 4.2 was introduced to the column, the compound was retained quantitatively on the column using flow rates in the range 5-20 cm^3 min^{-1}. The sorption efficiency of the foam column is slightly decreased by increasing the flow rate, but the extraction still reasonable even at 30 cm^3 min^{-1}. Azamethiphos (1.1 mg) was retained quantitatively on the foam column from aqueous solution adjusted to pH 11.5 at flow rates in the range 2-10 cm^3 min^{-1}. Elution of malathion was quantitatively effected with 50 cm^3 of either distilled water adjusted to pH 2.4 or acetone at 3-5 cm^3 min^{-1}. On the other hand elution of azamethiphos was achieved using 50 cm^3 of either distilled water adjusted to pH < 2 or acetone at 3-5 cm^3 min^{-1}.

As a consequence of the above characterization of column performance for malathion and azamethiphos, the separation of a mixture of these inseticides was tried. When a mixture containing 0.492 mg of malathion and 0.44 mg of azamethiphos in 25 cm^3 aqueous solution adjusted to pH 4.2 is allowed to percolate through foam column at 5 cm^3 min^{-1}. flow rate malathion is quantitatively retained on the foam column while azamethiphos moved with the solvent front. Malathion was then eluted with acetone. Preconcentration of malathion or azamethiphos in tap water was successfully carried out using the proposed foam column. One dm^3 of tap water spiked with malathion (0.492 mg) or azamethiphos (0.44 mg) and adjusted to pHs 4.2 and 11.5, respectively, were passed through the foam column at a flow rate of 5 cm^3 min^{-1}. The insecticides was then recovered quantitatively from the foam material with acetone.

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