Concentration of the Organophosphorus Pesticides: Fenchlorphos, Crufomate and Nogos in Water By Using Amberlite XAD-2

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(Received on 16/7 /2008) **(Accepted for publication 19/11 /2008)**

Abstract

The pollutants organophosphorus pesticides : fenchlorphos, crufomate and nogos in water are concentrated on a column of a macro reticular amberlite XAD-2 resin adsorbent and recovered by elution with acetonitrile, methanol and chloroform.

The distribution coefficient, K_d for chromatographic separation (adsorption and desorption }has been calculated for each pesticide with each solvent. This resin proved to be rapid and efficient for adsorption of these pesticides from water samples and acetonitrile or methanol are the best solvent for pesticides desorption due to powerful polarity of solvent as well as dielectric constant compared with chloroform .

We suggest simple relationship between the column void volume and volume of organic solvent needed to elute each pesticides quantitatively ; it has found that the best desorption obtained with optimal volume of acetonitrile or methanol equals to three to four times that of the adsorption column void volume, when the elution solvent allow to stand for one hour at a flow rate 1 ml./ min. .

The 30% Breakthrough capacity was calculated to check elute recovery for fenchlorphos, crufomate and nogos and found to be equals to 3330, 7030 and 19100 µg pesticides/ ml XAD-2 resin 3.45, 7.52 and 20.4 µg (pesticides) /mg XAD-2 resin respectively, which are inversely proportional to the molecular weight of these pesticides.

Concentration Factor (CF) is calculated and found to ranging from 1500 to 3000 which proved the accuracy of this method for being present at trace concentration of these pesticides in water samples.

الخلاصة

تم تركيز المبيدات العضوية الفسفورية فنكلورفس، كروفوميت و نوكوز الملوثة للماء باستعمال الراتنج amberliteXAD-2 الشبكي العياني واسترجاعها باستعمال المذيبات العضوية : نتريل المثيل، ميثـانول و كلوروفورم . تم حساب قيم معامل التوزيع K_d لعملية الفصل الكروماتوغرافي (الامتزاز و الابتزاز) لكـل مبيد ، وأظهر الراتنج كفاءة عالية و سرعة كبيرة لعملية امتزاز المبيدات من عينات المياه ، وأن نتريل المثيل أو الميثانول هما المذيبان الأفضل و الأكفأ لابتزاز المبيدات من الراتنج ويرتبط ذلك بقطبية و قوة المذيب و

ثابت العزل الكهربائي مقارنة مع الكلوروفورم.

تم اقتراح و تثبيت علاقة بسيطة بين الحجم الفضائي لعمود الامتزاز و حجم المذيب العضوي الـلازم لابتزاز المبيد كليا" ، ووجد إن أفضل ابتزاز لهذه المبيدات يمكن الحصول عليه باستعمال حجم مـن المـذيب العضوي نتريل المثيل أو الميثانول يكون مساويا من ثلاث إلى أربع أمثال الحجم الفضائي للعمود المستخدم عند ترك المذيب بتماس مع الراتنج لمدة ساعة واحدة وبمعدل جريان 1 مل/ دقيقة.

تم حساب سعة الراتنج عند نسبة 30 % من نقطة نزول المبيدات فنكلورفس، كروفوميـت و نوكـوز للتحقق من استرداد المبيد وكانت 3230 ، 7030 و 19110 مايكروغرام مبيد/ مل راتـنج XAD-2 ، أو 3.45 ، 7.52 و 20.4 مايكروغرام مبيد / ملغرام راتنج XAD-2 على التوالي والذي يتناسـب عكسيا" مع الوزن الجزيئي لهذه المبيدات، فضلا" عن حساب معامل التركيز والذي تراوح ما بين 1500 إلى 3000 والذي يؤكد دقة و كفاءة الطريقة في التركيز الواطئ للمبيدات في عينات الماء .

Introduction

Usually organophosphorus pesticides are present in water in such amounts that using a separatory funnel to carry out the extraction procedure is difficult because of the large volume of water needed to obtain meaningful data. For the determination of pesticides at lower concentrations , different methods are used, such as continuous extraction with organic solvents [1] or adsorption on charcoal [2] and others [3, 4]. These methods require long time to extract these pesticides using continuous extraction and recovering from the charcoal.

Amberlite XAD resins are available with a variety of polarities , XAD-1, XAD-2, XAD-4, XAD-7 and XAD-8 and numerous solvents of different polarities are available. The potential of these resins for the extraction and separation of organic compounds from complex aquatic environmental samples has yet to be fully realized . The adsorptive forces present when using amberlite XAD-2 resin as adsorbent are primarily of the Van deer walls type [5,6] . The amberlite XAD-2 resin beads are highly porous [7,8,9] . Size Exclusion Chromatography (SEC) was used as a clean-up procedure for organophosphorus pesticides fenchlorphos ,crufomate and nogos after extraction with the compatible solvent ethyl acetate [10]. The analysis studied of organophosphorus pesticides residue fenchlorphos ,crufomate , nogos, dursban, diazinon and malathion in food samples [11,12] . Amberlite XAD-2 resin has been used to concentrate dissolved organic materials from seawater [13] recover trace organics [14] and determination of chlorinated pesticides [15] from potable water. amberlite XAD-2 resin was used in OVS-2 filter/solid sorbent sampler tube to be adsorb organophosphorus pesticides [16] .

The purpose of this study was to develop a simple general method for the concentration of trace organophosphorus pesticides fenchlorphos , crufomate and nogos widely applied in IRAQ in water employing amberlite XAD-2 resin adsorbent.

Experimental

Materials

All compounds and solvents used were of high purity (A.R. grade) and the water employed was distilled water. Amberlite XAD-2 resin , 20-50 mesh was washed for 24 hours with absolute ethanol then sequentially wash with 0.1 N NaOH, distilled water, acetonitrile, methanol, and ethanol[17,18] to remove monomers and soluble, uncross-linked polymers, then

the purity of the resin was checked in blank procedure. The purified resin washed with distilled water and stored under distilled water. Pesticides were of technical grade purity.

Apparatus

A shimadzu 160 Uv-Vis double beam spectrophotometer with quartz cells size 1 cm were used to measure the absorbance at λ_{max} of each pesticides analyte at different solvents and a Corning 220 conductometer was used. The adsorption column was a (20 cm x 1 cm i.d) glass tube fitted at one end with a Teflon stopcock and with glass disc as a support for resin beads.

Column Preparation

The amberlite XAD-2 resin was allowed to swell for at least 24 hr. using appropriate volume of ethanol then washing with distilled water. Distilled water slurry of amberlite XAD-2 resin was slowly added to the column containing distilled water in order to prepare and pack a 10 cm resin column. The water sample was passed through the column, allowing the column to run dry in a stream of air at room temperature for 30 min. by attaching air tubing to the column delivery tip. A 50 ml of acetonitrile or methanol was added to the top of the column, and the beds were stirred to release the air bubbles and allow to stand for 1 hr. then eluted until 30 ml of elute were collected. After the solvent was allowed to run out of the column, the column flushed out with 350 ml of ethanol until a clear UV spectrum was obtained, followed by 350 ml of distilled water, until the water level was just at the top of the resin column, then the column was allowed to stand in water until it was used again.

Batch Equilibration for The Adsorption and Desorption:

Batch equilibration of amberlite XAD-2 resin for the adsorption and desorption (stripping) of pesticides was studied. The distribution coefficient, K_d of each pesticides on resin has been calculated by a batches method. A 10 ml of aqueous sample which contained 0.2 mg of pesticide was added to 0.27 mg of resin in a 25 ml glass test tube, shaken vigorously for 0.5, 2, 5 and 10 min., an aliquot of the aqueous layer was taken and analyses for the pesticide present. The percentage of pesticide sorbet was measured by Uv-Vis spectrometry, the concentration of each pesticide has been determined by reading the absorbance at the peak wavelength of the adsorption spectra. The sorbet pesticides was eluted (desorbed or stripping) from the resin with 2 ml of organic solvents acetonitrile, methanol and chloroform. Using micro syringe, a 100µl aliquot of the eluted (extraction) organic layer add to 3 ml of the same solvent was taken for analysis.

Results & Discussion:

The distribution coefficient, K_d has been calculated of adsorption and desorption as a function of the difference in the concentration of pesticide before and after achievement of equilibrium [19,20,21].

$$K_d = \frac{\text{Volume of Solution, ml}}{\text{Weight of dry resin, gm}} \times \frac{\text{Weight of Solute on the resin}}{\text{Weight of Solute in Solution}} \quad \text{ml./gm}$$

The wide variation in the K_d values for the different pesticides (table-1)[22,23,24] indicates that the resin dose not have the same preference for all pesticides.

Table-1: Physical and chemical properties of organophosphorus pesticides.

	Crufomate	***Fenchlorphos***	***Nogos***
Other name	Rulene	Ronnel	Dichlorvos
Empirical formula	$C_{12}H_{19}ClNO_3P$	$C_8H_8Cl_3O_3PS$	$C_4H_7Cl_2O_4P$
Structural formula	$(CH_3O)(CH_3NH)P(=O)O(C_6H_3)ClC(CH_3)_3$	$(CH_3O)_2P(=S)O(C_6H_2)Cl_3$	$(CH_3O)_2P(=O)OCH=CCl_2$
Chemical name	4-tert-butyl-2-chlorophenyl methyl phosphoramidate	o,o,dimethyl,o-2,2,5-trichlorophenyl phosphorothioate	o,o,dimethyl,2,2-dichlorovinyl phosphate
M. Wt., g /mole	291.2	321.5	220.9
L.D 50, mg / kg	950	1000-3000	56-80

Initial experiments demonstrated that the maximum K_d values were reached in 10 min. shaken time , a very rapid increase in K_d values was observed for equilibration time and reached steady state after 5 min.(Fig.–1) whereas in desorption, the opposite was occurred (Figs.- 2, 3, 4), the K_d values were found to be decreases sharply with the increasing of equilibration time and reached steady state after 5 min., then slow decreases in the K_d values. This resin proved to be rapid and efficient for adsorption of these pesticides from water samples and acetonitrile or methanol are the best solvents for pesticides desorption, due to powerful polarity of solvent as well as dielectric constant compared with chloroform (table-2)[25].In the adsorption process, the portion of the pesticide which has little affinity for water (hydrophobic) was preferentially adsorbed on the hydrophilic polystyrene surface of the pesticide will remain oriented in the aqueous phase, alteration in the hydrophobic/ hydrophilic balance within the solute or within the solvent mixture in comparison to the resin will be affect on the adsorption of the solute although the beads are highly porous, there is evidence which suggests that penetration of the pesticide into the interstices is minor and, therefore major adsorption is on the outer bead surface[19].

The void volume (for 10 cm resin columnx1 cm i.d)was determined by measuring the breakthrough[26] of 1 ml of 0.05 N NaCl using a Corning 220 conductometer (Fig-5), the void volume was calculate and found to be equals to 6 ml , the flow rate exceeding 20 void volume / hr caused a decrease in capacity [19] , then the flow rate of adsorption adjusted to approximately 2 ml./ min .

Table-2: Physical and chemical properties of organic solvents.

Solvent	*M.Wt. gm/mole*	*B.P, °C*	*Dielectric constant*	*Solvent Polarity ρ´*	*Solvent Strength °ε*
Acetonitrile	41.05	82	38.8	5.8	0.65
Methanol	32	64.7	32.6	5.1	0.95
Chloroform	119.4	61.26	4.8	4.1	0.40

Among the aims of this work , we suggest simple accurate relationship between the void volume of the adsorption column and volume of organic solvent needed to elute each pesticide quantitatively; when the elution solvent was directly passed through the column at 2 ml./ min. (method No. one) or the elution solvent allow to stand for 1 hr. and the flow rate was approximately 1ml./ min. (method No. two) , the comparison revealed the superiority of the method two over the method one, it has been found that the best desorption obtained with optimal volume of acetonitrile or methanol equals to three to four time that of the void volume, when the elution solvent allow to stand for 1 hour . (Figs- 6, 7, 8) .

The 30% Breakthrough capacity[27] was calculated to check elute recovery was found after 300, 630 and 1735 mL initial aqueous standard pesticide solution passing for the fenchlorphos, crufomate and nogos, and found to be equals to 3230 , 7030 and 19110 µg pesticide / ml XAD-2 resin or 3.45, 7.52 and 20.4 µg pesticide/mg XAD-2 resin respectively which are inversely proportional to the molecular weight of these pesticides at a flow rate of 2 ml. / min. (Fig.- 9)., the differences among 30% Breakthrough capacity apparently favors small size aliphatic over aromatic systems [9].

30% Breakthrough= {pesticide weight, µg / resin (column)volume, mL }

when the concentration of pesticide in the effluent solution divided by the concentration of pesticide in the standard feed solution reached 0.3.

Column volume = 3.14 x $(\text{radius})^2$ x resin height

Concentration factor (CF) is calculated and found to ranging from1500 to 3000, these values proves the sensitive of the method for being present at trace concentrations in water samples.

CF = { feed sample passed, mL / volume of pesticide product, mL (organic solvent) }

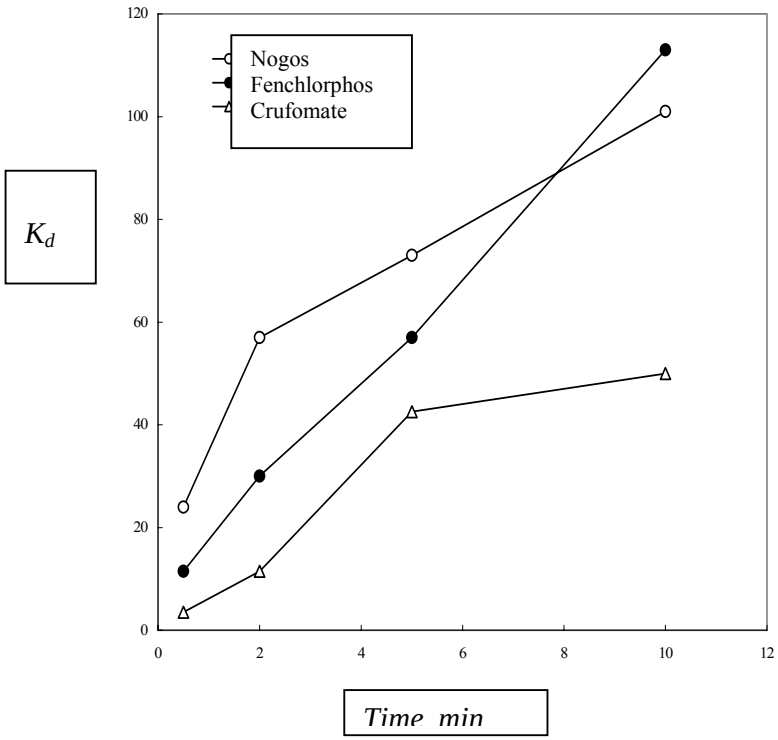

Fig. 1: Distribution coefficient K_d for adsorption process of organophosphorus pesticides fenchlorphos , crufomate and nogos at 10 ppm on amberlite XAD-2.

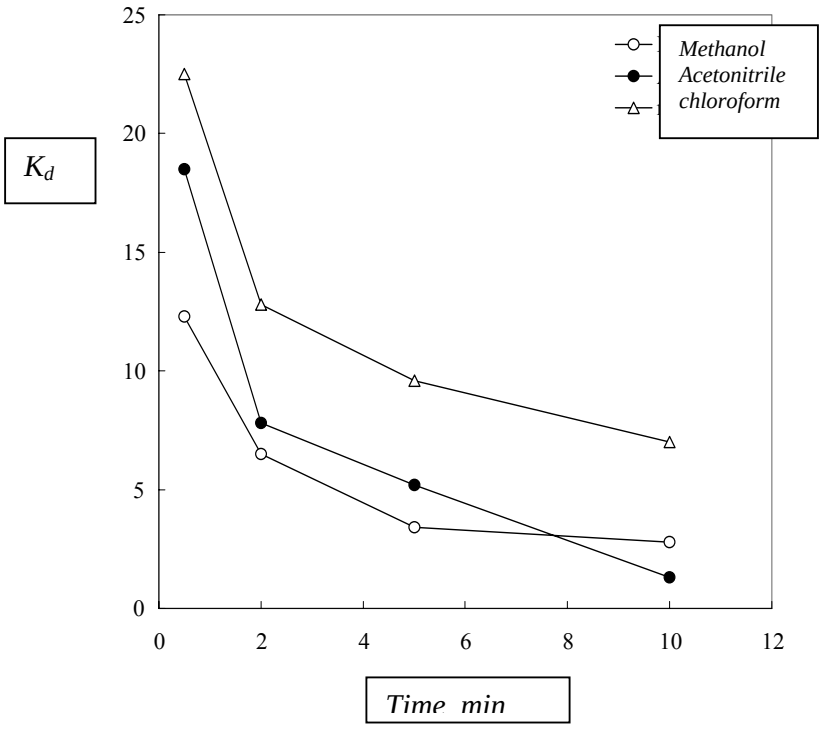

Fig. 2: Distribution coefficient K_d for desorption process of fenchlorphos from *amberlite XAD-2 with different organic solvents.*

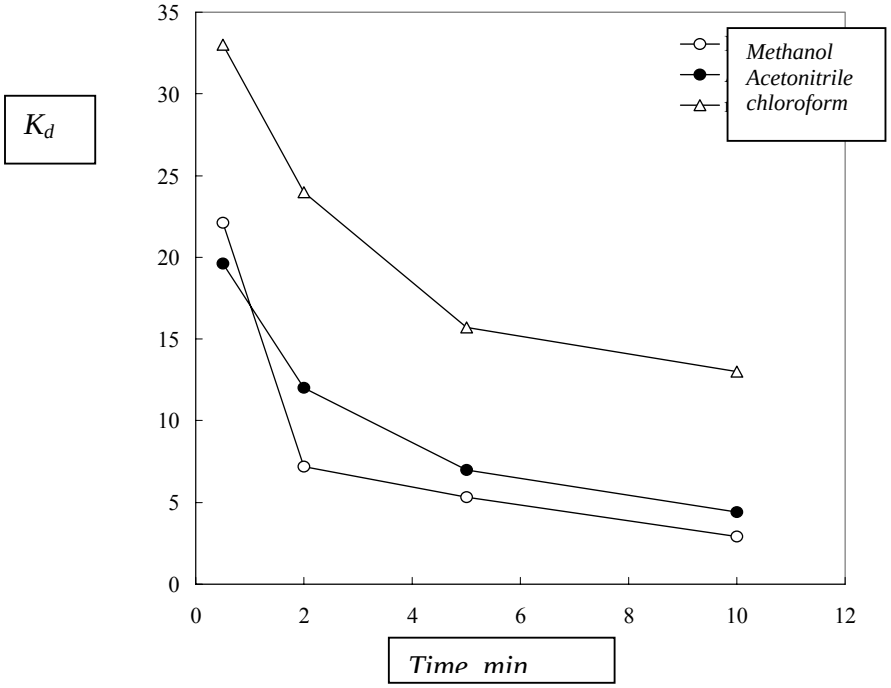

Fig. 3: Distribution coefficient K_d for desorption process of crufomate from amberlite XAD-2 with different organic solvents.

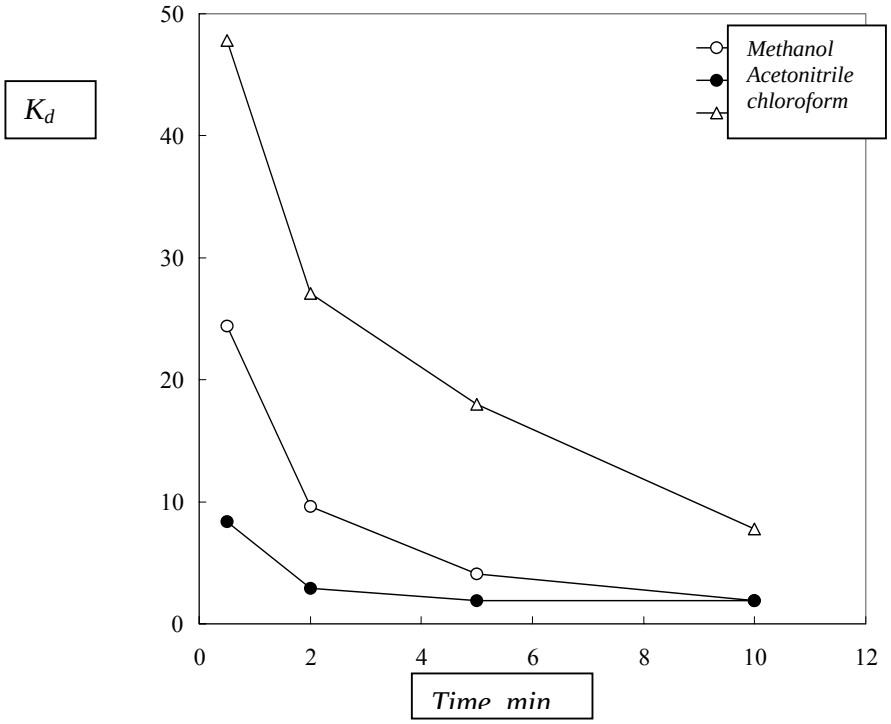

Fig. 4: Distribution coefficient K_d for desorption process of nogos from amberlite XAD-2 with different organic solvents.

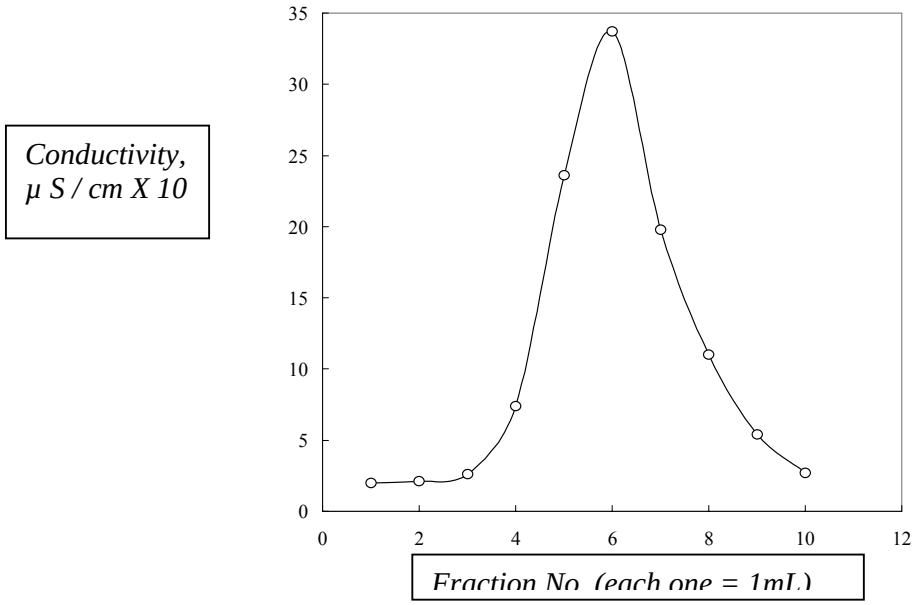

Fig. 5 : The void volume of (10 cm X 1 cm i.d.) , amberlite XAD-2 column

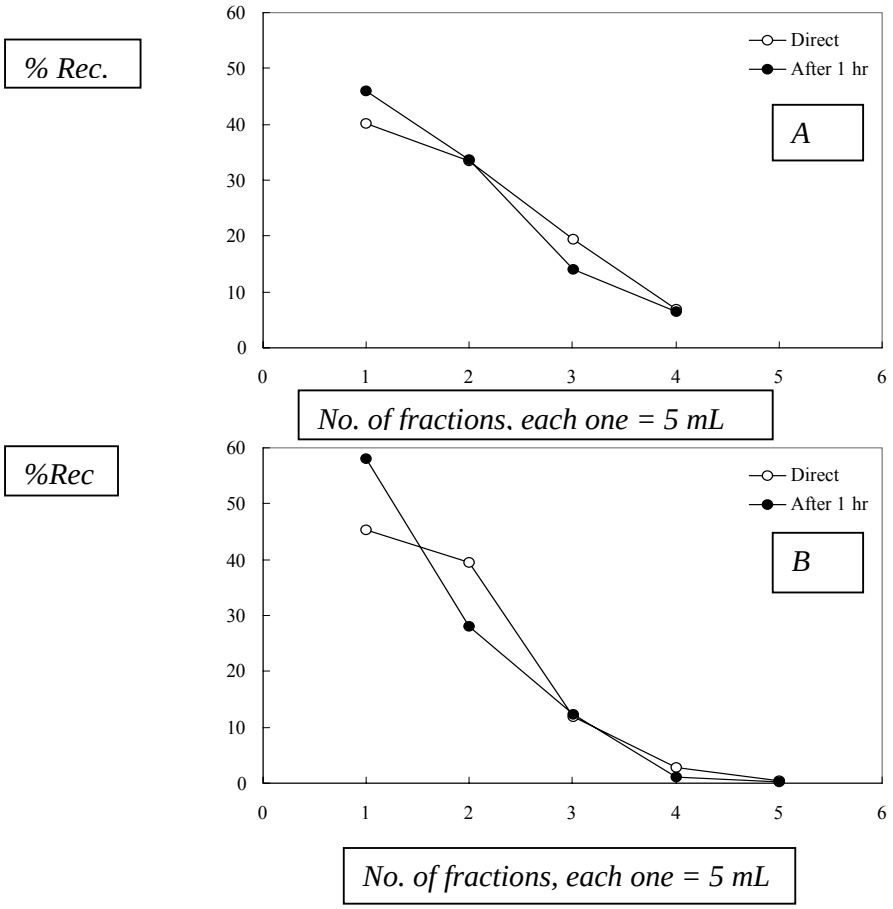

Fig. 6: Elution of fenchlorphos from(10 cm X 1 cm i.d.) amberlite XAD-2 column With : A) acetonitrile and B) methanol.

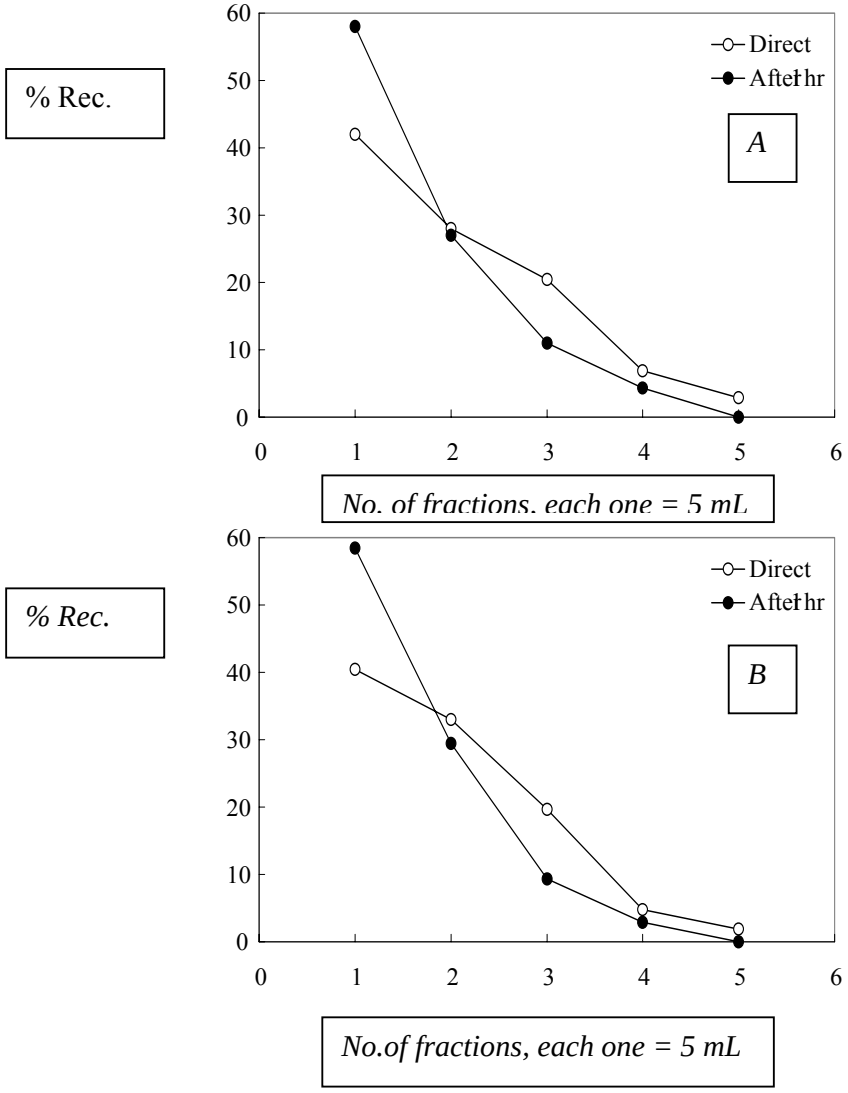

Fig.7: Elution of crufomate from (10 cm X 1 cm i.d.) amberlite XAD-2 column with : A) acetonitrile and B) methanol.

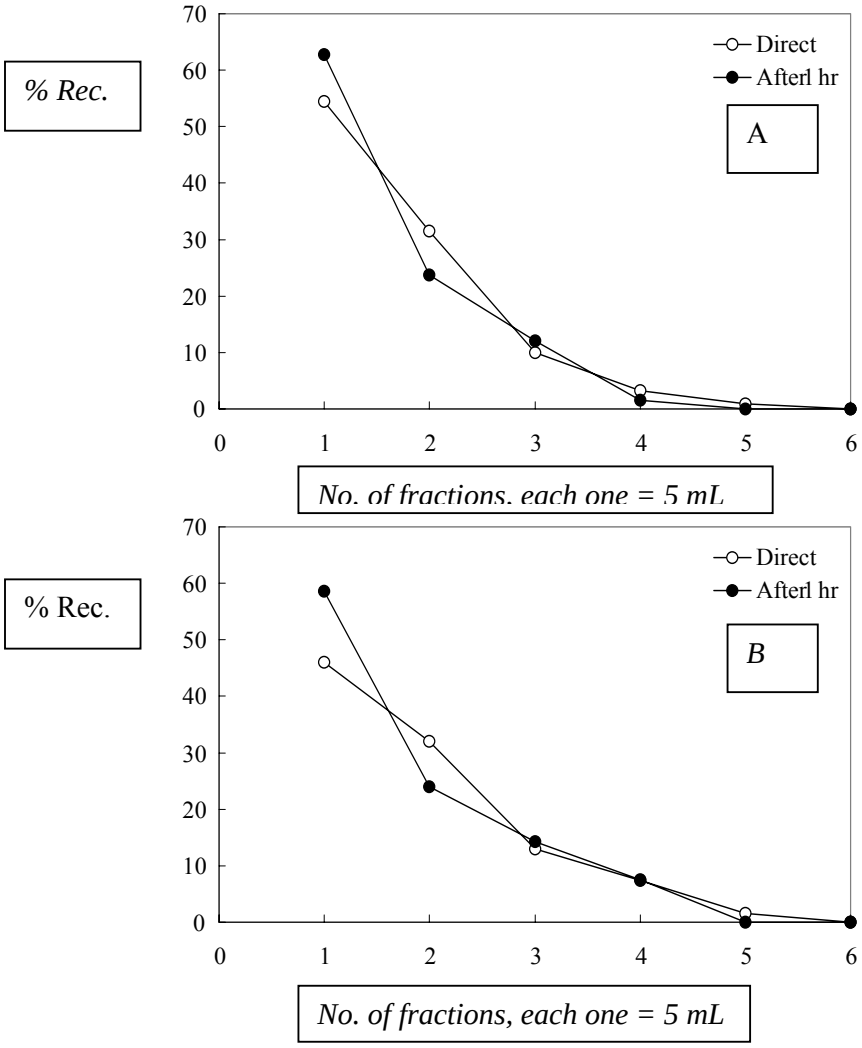

Fig. 8: Elution of nogos from(10 cm X 1 cm i.d.) amberlite XAD-2 column With: A) acetonitrile and B) methanol.

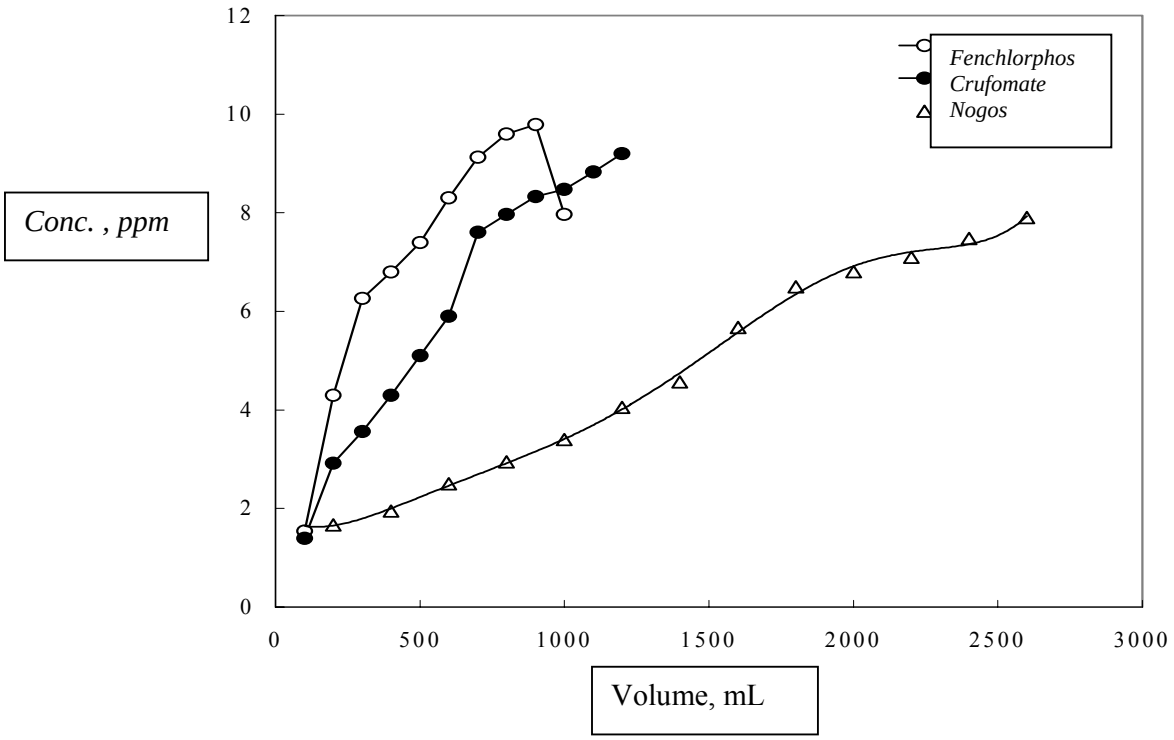

Fig.9: 30% Breakthrough capacity of fenchlorphos, crufomate and nogos from (5 cm X 1 cm i.d.) amberlite XAD-2 column.

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