



DETERMINATION OF CARBOFURAN IN WATER SAMPLES BY SOLID PHASE EXTRACTION With β - CYCLODEXTRIN POLYMERS AND HPLC/ UV ANALYSIS

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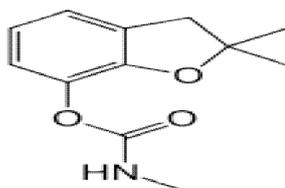
ABSTRACT

Cyclodextrins are type of oligosaccharide consisting of glucose units. Three types of cyclodextrins namely α , β and γ - consist of six, seven and eight glucose units respectively joined with α -1,4-glycosidic linkage. β - cyclodextrin is most useful, very stable and low priced oligosaccharide. Host-Guest inclusion complexes can be formed by inclusion of host in the cavity of cyclodextrin polymers. β - cyclodextrin is modified with cross-linker 1,4-butanedioldiglycidyl ether to form polymer. This polymer was used as a sorbent for the solid phase extraction of carbofuran from various water samples and then samples were analysed with the help of HPLC. For quantitative extraction ($\geq 95\%$) of carbofuran with β - cyclodextrin polymer different parameters like pH, amount of sorbent, contact time, sample solution volume, and volume of eluent were optimized. The HPLC analysis of carbofuran was done at λ_{\max} at 272nm using 40:60 acetonitrile: water as a mobile phase with a flow rate 1.4ml/min. LOD is 38.0ng/ml and 127.0ng/ml and LOQ is 0.127ng/ml. Relative standard deviation is 2.02%. The developed method was applied successfully for the determination of carbofuran in various water samples.

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INTRODUCTION

Pesticides are largely used in agricultural and non agricultural practices throughout the world. These pesticides had been categorized into different categories depending on their use and structure. Their persistent nature makes soil, water and food contaminated with these toxic chemicals [1-2]. These hazardous chemicals enters into the body through ingestion, inhalation and by direct contact. These toxic chemicals pose a great threat to living beings, environment and thus causing ecological imbalance [3-10]. N-methylcarbamates were introduced in early 1950s as pesticides. Carbofuran 2,2-dimethyl-2,3-dihydro-7-benzofuranyl-N-methylcarbamate is a most toxic carbamate insecticide. It belongs to a class of namaticides and acaricides on the basis of its use.



It is largely used for protection of crops like corn, potato, soyabean etc. as it is highly toxic to different classes of insects.

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Water gets easily contaminated with this insecticide by its use on agricultural crops due to its high solubility (350 mg/L at 25°C). It is systemic insecticide means it accumulates in different parts of a plant through roots. Carbofuran is highly toxic to the environment as well as human health due to its high solubility. Carbofuran enters into the body through ingestion, inhalation and by direct contact. Carbofuran affects the nervous system in humans by inhibiting the neurotransmitter acetylcholinesterase (AChE). It prevents the transmission by breakdown and blocking of acetylcholine transmitter. [11]

Determination of trace levels of carbamates in water is a challenging task for analytical chemist so there is need of sensitive, rapid, selective analytical technique to analyse the trace levels of carbofuran in water sample. A highly efficient preconcentration and clean up method is required prior to analytical technique to improve the limit of detection of the instrument and to get maximum recovery of the analyte. Different extraction techniques for the extraction of the insecticides in various matrix were used like liquid-liquid partition [12-14], solid phase extraction [15-17], SFE [18-19], SBSE [20] etc. For solid phase extraction various sorbents like C₁₈ [21-23], Silica gel [24] Diatomaceous earth material [25-26], XAD[27], polymers like polystyrenedivinyl benzene [28], activated carbon [29-30], multi walled carbon nanotubes [31-32] and cyclodextrin [33-35] were used. After extraction various common chromatographic techniques for

determination of these insecticides like GC [36-37], HPLC [38-39], UPLC [40-41], capillary electrophoresis [42-43], Spectrophotometry and voltametrically [44-45] etc. were used. The determination of pesticides especially polar pesticides with GC is difficult because before determination with GC, there is need of derivatisation or hydrolysis of the analytes but no such derivatisation is required in case of HPLC. So the combination of SPE with HPLC is highly sensitive and selective technique for the determination of trace levels of pollutants in environmental samples [46]

So in my work, solid phase extraction of carbofuran was done with β -cyclodextrin polymer from water by using HPLC as an analytical technique.

β -Cyclodextrin (β -CD) is a stable oligosaccharide which is composed of seven glucose units linked together by α -(1,4)-glycosidic linkage. This linkage generates a cavity in which it can incorporate the guest molecule to form host-guest inclusion complexes. Polymers are formed by covalent linkage of two or more β -Cyclodextrins. These β -cyclodextrin polymers had been used for the solid phase extraction of various analytes. Here, we have developed a relatively easy, sensitive rapid, and selective method for the solid phase extraction of Carbofuran by using HPLC-UV as an analytical technique. In this acetic acid/sodium acetate buffer solution of pH 6.0 was used for effective extraction of this insecticide. Carbofuran gets efficiently sorbed on β -CDP that can be recovered with the help of eluent for determination.

Experimental

Materials

HPLC grade water and all solvents were used throughout the experiment. Carbofuran (99.9%) and 1,4-Butanediol diglycidyl ether were obtained from Sigma Aldrich Company (U.S.A.). β -Cyclodextrin was obtained from SD fine chemical India private limited (Mumbai). Buffer solutions used were hydrochloric acid/ sodium acetate for pH 2.0-3.5, sodium acetate/acetic acid for pH 4.0-6.5, ammonia/ammonium chloride for pH 8-9. Glasswares were washed with chromic acid and soaked in 5% nitric acid and rinsed with double distilled water.

Instruments

HPLC (Waters 515) pump equipped with C-18 column (5 μ m) of 4.6 internal diameter and 21mm length attached with UV-detector. All pH measurements were performed using Digital pH-meter (Toschkon-Toshniwal) with a combined glass electrode. A mechanical shaker, ultrasonicator etc. were used to carry out all the inclusive procedures.

Procedure

Synthesis of the β -Cyclodextrin polymer (β -CDP)

A known method was used to synthesize β -CDP [47]. 20 g of β -CD was taken and dissolved in 50 ml of 20% NaOH. Then 20 ml of 1,4-butanediol diglycidyl ether was added drop wise with continuous stirring on magnetic stirrer. The polymer was formed in 1.5 h and dried at 90 °C. The polymer was grounded, sieved and washed with double distilled water for 5-6 times. After this, the polymer was dried again at 90°C and kept at room temperature in a dessicator.

Preparation of standard solutions

Stock solution was prepared by dissolving 0.050g of Carbofuran in 50ml of acetonitrile and stored in stained glass stopper bottles at 4°C. Standard working solutions of Carbofuran were prepared daily by appropriate dilutions of aliquots of the stock solution in acetonitrile.

Batch extraction procedure

β -CDP and 10.0 ml of buffer solution (pH 6.0) were added to a 250 ml stoppered conical flask at room temperature. The mixture was allowed to stand for approximately 15 min for sufficient swelling of β -CDP. 10 μ g/ml of carbofuran was added and made the volume up to 100 ml with water. Then the mixture was shaken for 60 min. in the mechanical shaker for the maximum uptake of the analyte by the polymer. After that the sample solution was filtered with whatman filter paper and the analyte was eluted with the help of 6.00ml of acetonitrile. The % uptake was analyzed with the help of HPLC at 272 nm using 40:60 ACN: water as a mobile phase with a flow rate 1.4ml/min.

Sample collection and conditioning

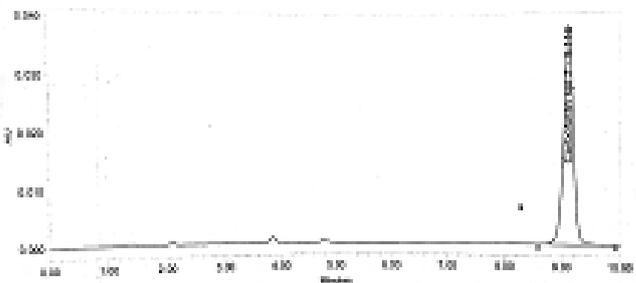
Water samples were collected from the different sources. Cellulose membrane filter (0.45 nm pore size) was used for immediate filtration of the water samples and samples were stored in pre-cleaned polyethylene bottles. After then, pH (6.0) of the samples was adjusted and the preconcentration procedure as described above was applied.

Analytical Performance

At room temperature the column of HPLC was operated isocratically using 40:60 (v/v) acetonitrile: water as a mobile phase with a flow rate 1.4ml/min. An aliquot of 20 μ L was injected into the column. The mobile phase was filtered through a 0.25 μ m nylon membrane filter. With this mobile phase carbofuran could be completely separated from the matrix influences at retention time R_t = 9.1min. LOD is 38ng/ml and LOQ is 127.0ng/ml. RSD is 2.02%.

The concentrations of carbofuran were calculated by calibration with the peak areas of different standards of carbofuran used.

HPLC of Carbofuran



RESULTS AND DISCUSSIONS

Effect of pH

The sorption of the analyte on the polymer is dependent on the pH of the sample solution due to the presence of hydrogen ions in the solution. 10 μ g/ml of carbofuran was spiked to a 100ml of sample solution. The pH of the solution was adjusted from 2-9 by using different buffer solutions and then the

preconcentration procedure described above was applied. As the maximum recovery ($\geq 95\%$) was obtained at pH 6.0 (Fig.1). Therefore the pH 6.0 was chosen for further optimization.

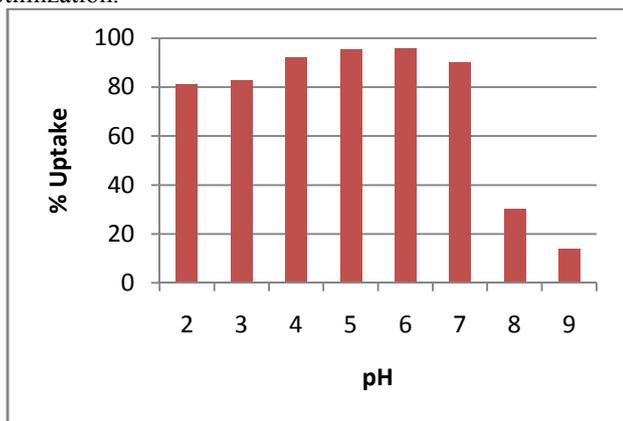


Fig.1 Effect of pH on the uptake of Carbofuran on β -CDP [10 $\mu\text{g/ml}$ of Carbofuran; 200mg of the sorbent; 100ml sample volume]

Effect of shaking time

Shaking time is another important factor in determining the possibility of application of the β -CDP polymer for the selective and sufficient uptake of carbofuran. The %age uptake of carbofuran by β -CDP polymer was studied for different shaking time (10-80min.). The results showed that %age uptake of carbofuran reach maximum ($\geq 95\%$) at 60 min. (Fig. 2). Therefore, the shaking time of 60 min. was selected as the adsorption equilibrium time.

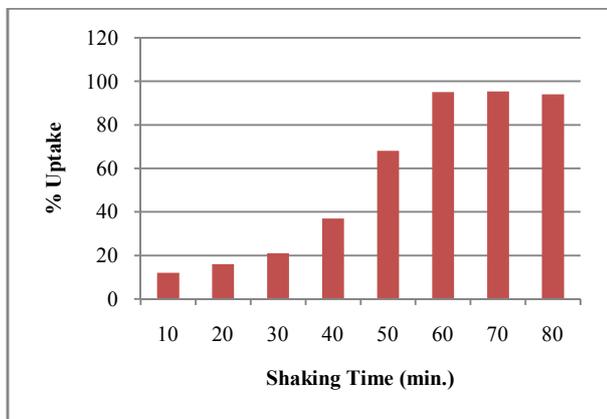


Fig 2 Effect of shaking time on the %age uptake of Carbofuran on β -CDP [10 $\mu\text{g/ml}$ of Carbofuran; pH 6.0; 200mg of the sorbent; 100ml sample volume]

Effect of the amount of sorbent

Amount of sorbent is an important factor to make method more efficient so that maximum recovery of carbofuran can be obtained by using minimum amount of the polymer. For this different amount of polymer (100mg to 500mg) was investigated by the above described procedure. Results showed that %age uptake increases but after 200mg the increase is very small (Fig. 3) so amount of polymer i.e. 200mg was selected for further.

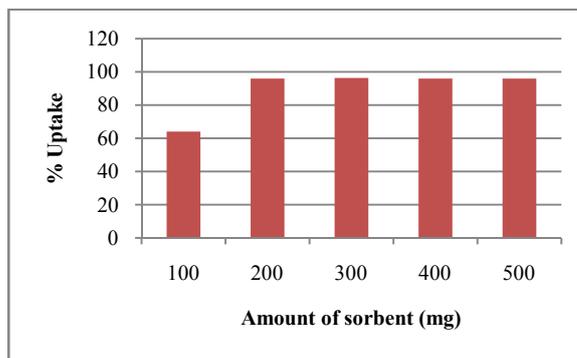


Fig 3 Effect of the amount of polymer on the uptake of Carbofuran on β -CDP [10 $\mu\text{g/ml}$ of Carbofuran; pH 6.0; contact time 60min. ; 100ml sample volume]

Effect of the sample solution volume

The effect of sample solution volume on the maximum %age uptake of carbofuran was investigated in order to explore the possibility of enriching low concentration of analytes from large volume of solution. A range of 25- 300ml of sample solutions containing 10 $\mu\text{g/ml}$ of carbofuran were taken for this purpose. Quantitative uptakes were obtained for sample volume of ≤ 150 mL (Fig. 4). Therefore, 100 mL of sample solution was adopted for the preconcentration of analyte from sample solutions.

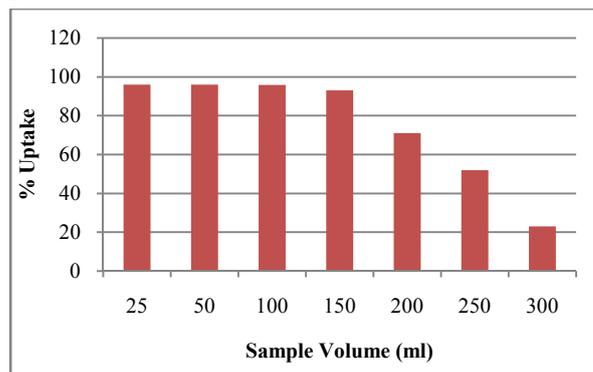


Fig 4 Effect of the sample volume on the uptake of Carbofuran on β -CDP [10 $\mu\text{g/ml}$ of Carbofuran; pH 6.0; contact time 60min. ; 200mg of sorbent]

Effect of eluent volume

Eluent volume ranging from 1-10ml with 1ml/min. flow rate was investigated for the elution of carbofuran from the polymer. The experimental outputs showed that quantitative recovery ($\geq 95\%$) was obtained with 6ml (Fig. 5) of the eluent i.e. acetonitrile. Therefore, 6.0 ml of acetonitrile was used for eluting carbofuran from the polymer.

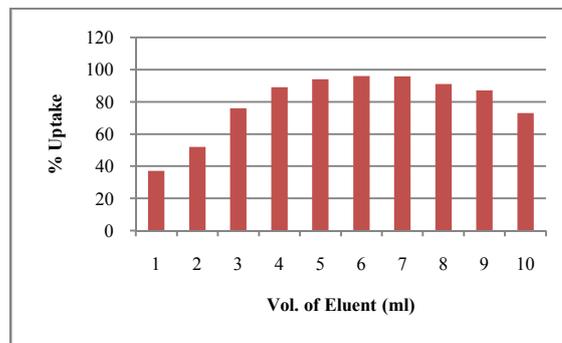


Fig 5 Effect of the eluent volume on the uptake of Carbofuran on β -CDP [10 $\mu\text{g/ml}$ of Carbofuran; pH 6.0; contact time 60min.; 200mg of sorbent; 100ml sample volume]

Determination of Carbofuran in different water samples

Sample	Spiked (ng/ml)	Found (ng/ml)	% Recovery
Tap Water	0.0	N.D.	-----
	200.0	192.0	96.0
	170.0	162.0	95.3
Surface Water	0.0	N.D.	-----
	190.0	183.0	96.3
	140.0	134.0	95.7
Mineral Water	0.0	N.D.	-----
	180.0	172.1	95.6
	150.0	143.1	95.4

CONCLUSION

The developed method of preconcentration is simple and reliable for the quantitative recovery of carbofuran in various water samples. Carbofuran can be easily preconcentrated due to the great inclusion capacity of cyclodextrin polymers. The method of preparation of polymer is simple, rapid, easy and reliable. The prepared polymer is stable and can be used repeatedly. The developed method has a good selectivity, sensitivity and accuracy. The method is very convenient and can be easily applied to different water samples.

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