NEW SORBENT FOR CARBAMATE DETERMINATION IN PESTICIDES

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Abstract

Carbamate pesticides is one of the most dangerous organic compounds in the environment. In parallel with strict regulation and control of organic contaminants, there is an emerging trend of analytical determination and development towards finding an environmentally friendly pre-concentration technique. Microextraction methods are steps in this direction. In the current study, a new FND-CHF polar sorbent was proposed for the extraction of carbamate pesticides from aqueous medium. The functional groups on the nanodiamonds which have higher electrostatic interaction with the target analytes enhance the efficiency of this method as compared to the unmodified polypropylene hollow fiber. The factors that affect the preconcentration efficiency were studied and optimized. Gas chromatography-Mass spectrometry (GC-MS) technique was selected to determine the target analytes after on-column derivatization. Under the optimum conditions, the extraction efficiency of the novel method was high, with detection limits in the range of 0.044 to 0.084 µg.L-1. The reproducibility of extraction devices used for these experiments was satisfactory (relative standard deviations ranged from 3.4% to 7.7%). This indicates that this technique is excellent for routine analysis of environmental samples. The proposed novel technique gives an added advantage of reducing solvent consumption. Furthermore, the devices are inexpensive and can be prepared easily.

Keywords: Carbamate, Microextraction, Nanodiamond, Pesticides

1. Introduction

Pesticides are group of compounds either naturally occurring or synthesized chemically that are mainly required to block the dangerous effect of different type of insects, fungi, weeds and pests onto the agriculture products [1]. They also include molluscicides, fungicides, nematicides, herbicides, insecticides and rodenticides as well as plant growth regulators [1]-[4]. The World Health Organization (WHO) as well as Food and Agriculture Organization (FAO) classified the pesticides as a hazard's material [5], [6].

Carbamate pesticides are highly effective broad-spectrum pesticides. They are able to kill different types of insects simultaneously [7],[8]. This is referred to its relatively lower environmental persistence and higher effectiveness in eradicating pests [7]-[9]. However, their ability to inhibit acetylcholinesterase (AChE) activity in nervous system is of tremendous concern, in which the AChE increase the hydrolysis rate of the neurotransmitter acetylcholine (ACh) to acetic acid and choline. Cholin is an essential nutrient for the human body. Thus, carbamate pesticides are considered to be toxic [9],[10].

A few analytical techniques were used for the pesticides analysis includes gas chromatography-mass spectrometry (GC-MS) [11],[12], micellar electrokinetic chromatography (MEKC) [13], enzyme-linked immunosorbent assays (ELISAs) [14],[15], high performance liquid chromatography (HPLC) [13],[16]. Liquid chromatography (LC) [10],[17] and liquid chromatography coupled with mass spectrometry (LC-MS) [18]-[20] have been conducted for the identification and quantification of low concentration of carbamates in different samples.

HPLC with different detectors is one of the most familiar technique for the carbamate analysis [10]. But it's challenged by GC methods, because carbamates are thermal instability compounds, it needs some modification into thermally stable derivatives. While the GC-MS, which has higher sensitivity and selectivity, is chosen in this work instead of HPLC because carbamate pesticides presented in real water sample is in trace level. Therefore, derivatization has to be performed for GC-MS analysis to increase the hydrophobicity of carbamate pesticides to make the compound more volatile prior to chromatography analysis. Compared to other derivatization techniques, on-column derivatization is rather simple and is a rapid one-step approach [21].

Many preconcentration techniques were used for the analysis of pesticides including traditional liquid-liquid extraction (LLE) as well as solid phase extraction (SPE) [22],[23]. The LLE has been used to improve the elimination of interferences from the analyte a matrix on the pesticide pre-concentration. Also, to minimize the amounts of chemical solvents required, the SPE has been implemented using a cartridge filled with a suitable stationary phase for the liquid chromatography (LC).

Recently, different microextraction methods which consume less organic solvent than traditional extraction techniques have been used to extract organic polar analysts like carbamate pesticides from different environmental aqueous samples. These microextraction methods include solid-phase microextraction (SPME) [24], stir-bar-sorptive extraction (SBSE) [25] and liquid-phase microextraction (LPME) [26]. However, there are a few limitations for each extraction technique mentioned above when it was used to the preconcentrate of carbamate pesticides. SPME is expensive and the lifetime for the fiber is relatively short. LPME gives limited choices of water-immiscible polar solvents to extract polar compounds. Also, the only commercially available SBSE device is coated with polydimethylsiloxane (PDMS).

In this work, a new polar novel sorbent was developed namely FND-CHF. I used this sorbent to achieve low detection limits and to check its applicability onto trace environmental analysis.

2. Experimental Part

2.1. Chemical and reagents

Pure methanol (HPLC-grade) was bought from J.T. Baker (Phillipsburg, NJ, USA). The deionized water was prepared and collected on a Nanopure (Barnstead, Dubuque, IA, USA) water purification system. The five target analytes of carbamates as shown in Fig. 1 (purity 99% of each) were provided by the Chem-Service (West Chester, PA, USA). 0.2M

Trimethylphenylammonium hydroxide (TMAH) in methanol was purchased from Supreco (Bellefonte, PA, USA). The name and chemical structures of the target analytes in this study are shown in Table 1. 1000 $g.mL^{-1}$ of each compound was prepared in methanol as stock solution. The prepared solutions were stored in the refrigerator at 4°C. The real environmental water samples were collected from the local agricultural well located on Al-Burg Village in Hebron City-Palestine.

2.2. Instrumental

A QP-2010 GC-MS technique coupled with an AOC-20i autosampler provided by (Shimadzu, Tokyo, Japan) and the DB-5MS capillary column made from fused silica (30 m × 0.25 mm i.d., 0.25 μm film thickness) provided from J&W Scientific (Folsom, CA, USA) were used. The stationary phase used was made from 95% polymethylsiloxane. The mobile phase (ultra-pure Helium) was used at a flow rate of 1.70 $ml.min^{-1}$. The temperature programme was employed as follows: initial temperature of 60^{o}C for 2 min, then increased to 260^{o}C at 10^{o}C.min^{-1}, and held for 2 min. Temperature of the injector port was 270^{o}C. All injections were conducted by splitless mode. The column oven temperature used was 60^{o}C. For the parameters of mass spectrometer, the ion source temperature was set at 200^{o}C, and the GC-MS interface temperature were fixed at 280^{o}C. A mass range of mass over charge ration (m/z) from 50 to 500 was scanned to identify the retention times of each target analyte. To confirm the target pesticide, selected-ion monitoring (SIM) with higher sensitivity was used to identify ions. Two fragment ions were monitored (characteristic and molecular) ions for each analyte: chlorpropham (m/z of 227 and 185); propham (m/z of 193 and 151); carbaryl (m/z of 158 and 115), methiocarb (m/z of 182 and 167) and promecarb (m/z of 164 and 149).

A micro-syringe of 10 μL capacity was used for both derivatization and injection of sample into the GC-MS. After preconcentration, 1 μL of the extract was withdrawn into the micro-syringe followed by addition of another 1 μL of the derivatization reagent (TMAH) into the same micro-syringe immediately. The final 2 μL mixture was then directly injected into the GC–MS for analysis.

2.3 Functionalized-Nanodiamond coated hollow fiber.

The polypropylene (PP) hollow fiber membrane (600μm i.d., 200μm wall thickness, 0.2μm pore size) was supplied by Membrana (Wuppertal, Germany). A nanodiamond was purchased from International Technology Center (ITC) with 98 % purity. The average primary particle size of the nanodiamond was 4 nm. The as-received nanodiamond agglomerated in water suspensions with particle sizes around 200 nm. The nanodiamond was first undergoing oxidative purification. This was achieved by rapid heating the nanodiamond in a tube furnace in ambient air at atmospheric pressure at 425^{o}C for 7 hours. This was followed by functionalization the nanodiamond surface chemically via strong acid treatment. The procedure consists of the oxidative purified nanodiamond heating in a 9:1 mixture of concentrated H_2SO_4 and HNO_3 at 75^{o}C for 72 hours, then in 0.1M NaOH aqueous solution at 90^{o}C for 2 hours, and in 0.1M HCl aqueous solution at 90^{o}C for 2 hours. The resulting

diamond was extensively rinsed with deionized water and separated by sendimentation with a centrifuge at 15000 rpm and dried in vacuum.

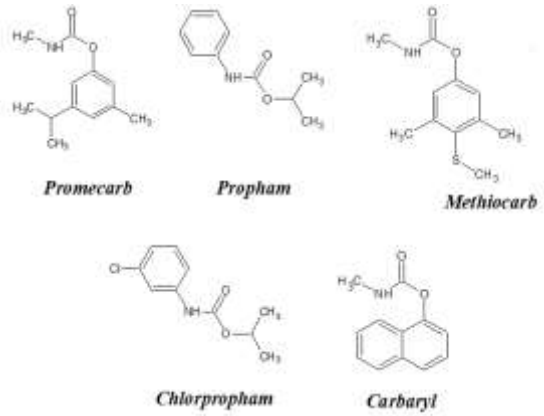
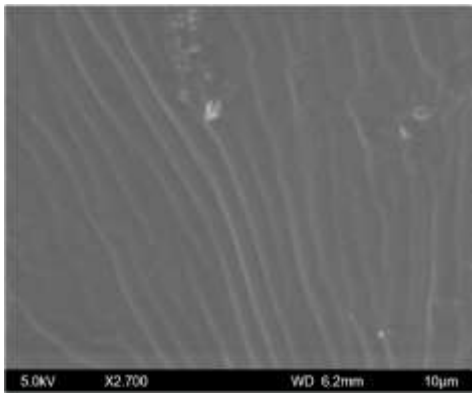
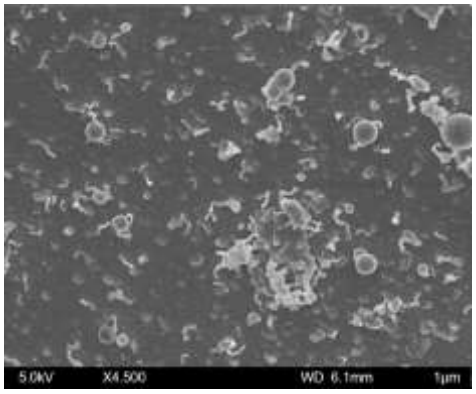


Fig. 1: Chemical structures of five target analytes of carbamate



(a)



(b)

Fig. 2: SEM image of PP hollow fiber coated with (a) PDMS only (b) PDMS with functionalized nanodiamond.

The nanodiamond was mixed with the polydimethylsiloxane (PDMS) before coated on the surface of PP hollow fiber. Curing agent was added to the mixture to help in drying. Fig. 2 shows the SEM image of PP hollow fiber coated with thin layer of PDMS (a), and PP hollow fiber coated with PDMS with functionalized nanodiamond (b). The SEM images show that

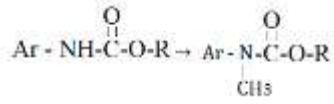
the surface of PDMS modified hollow fiber was smooth compared to surface of the coated hollow fiber by both PDMS and functionalized nanodiamond.

2.4 Extraction Process

To evaluate the performance of FND-CHF. Six pieces of FND-CHF were used. The fibers are tied together and placed inside the standard analyte solution as shown in Scheme 1. The solution is stirred using magnetic stirrer bar. The fibers are allowed to move freely in the solution. After a preset time, the fibers are taken out and desorb in 100µL organic solvent, methanol, with the assistant of sonication. The organic solvent that contains the analytes was directly injected into the GC-MS.

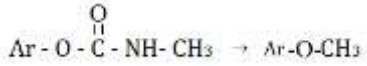
2.5 On-column Derivatization of carbamates

Carbamate pesticides are non-volatile polar compounds. Directly injection of carbamate pesticides into GC-MS would lead to their breakdown to amines and phenols. Thus, a derivatizing reagent, Trimethylphenylammonium hydroxide (TMAH), was used to derivatize carbamates in this project [21]. TMAH is an esterification reagent used to form aryl and methyl derivatives, especially of molecules having replaceable protons attached to nitrogen or oxygen like carbamates. TMAH is a strong base which can extract acidic alpha protons from carbamates to yield resonance-stabilised enolate anions and aryl or methyl group is than attached to the enolate anions. The ways are shown below [27].



Way I: for arylcarbamates

Way II: for N-methylcarbamates



3. Results and Discussion

Before applying the novel method to the real environmental samples, the extraction efficiency for the FND-CHF was optimized to obtain maximum analyte recovery by investigating various factors which include the volume ratio of extract to derivatizing reagent, extraction time, desorption time, salting-out effect and pH range. The preconcentration efficiency was evaluated based on the areas of the peaks produced from the GC-MS chromatograms.

3.1 Volume ratio of extract to derivatizing reagent (TMAH)

The volume ratio of extract to derivatizing reagent, TMAH, was investigated by injecting the mixture into the GC-MS directly without extraction process. This is to find out the optimum volume of derivatizing reagent that can give maximum derivatized product of carbamates and avoid the waste of derivatizing reagent used. From Fig. 3, it was observed that the volume

ratio 1 of extract to 2 of TMAH gives maximum peak area for the majority of carbamate compounds. When less derivatizing reagent used, the process of derivatization for all carbamates was not completed. When excess derivatizing reagent used, the total volume of mixture injected into GC-MS was increased and thus the analytes were diluted and resulting in smaller peaks observed. Therefore, 1:2 volume ratio of extract to TMAH that gave maximum peak areas was adopted.

Scheme 1. Experimental set-up for FND-CHF

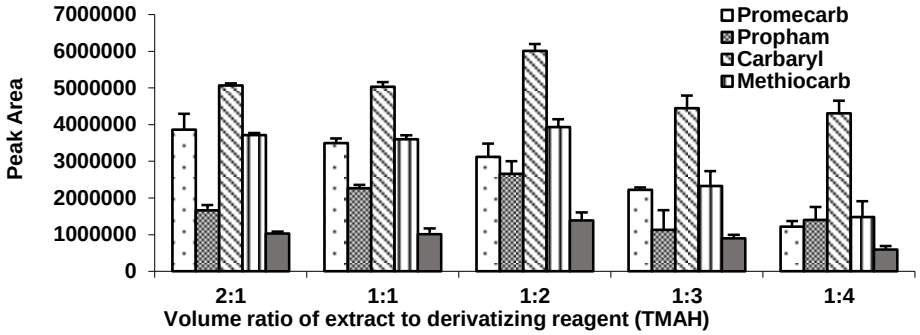


Fig. 3: The effect of volume ratio of extract to derivatizing reagent (TMAH)

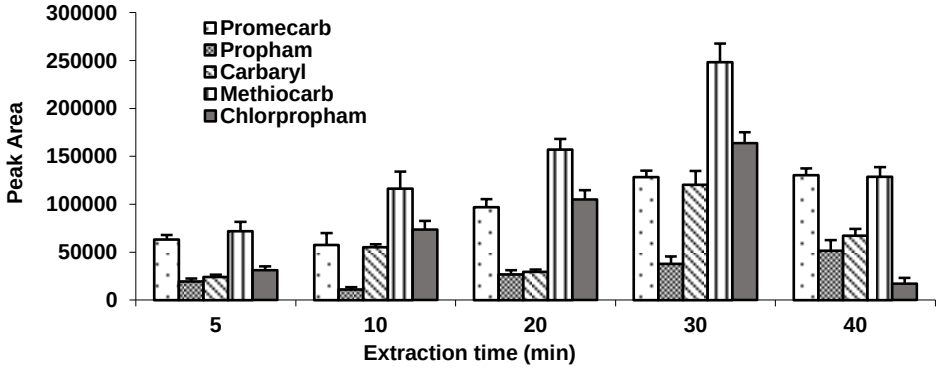


Fig. 4: The extraction time effect on the extraction efficiency for FND-CHF.

3.2 Extraction time

The optimized extraction time was investigated by extracting 50µg.L^{-1} carbamate mixture. The extracting time evaluated was from 5 to 40 minutes for FND-CHF. From Fig. 4, it was

observed that the extraction efficiencies improved as the exposure time was increased and then decreased after a certain time. This is because the extraction method is non-exhaustive, which means that the adsorption of the analytes onto the sorbent is based on equilibrium and desorption might occur as the extraction time increased. So, in this case, the efficiency of extraction depends on the mass transfer of the carbamates into the sorbent. The maximum peak area obtained was generally 30 minutes. Therefore, 30 minutes extraction time was adopted throughout the experiment.

3.3 Desorption time

The optimized desorption time was investigated by extracting 50µg.L^{-1} carbamate mixture. Desorption time evaluated was from 5 to 30 minutes for the sorbent. As reported previously, the suitable solvent used for desorption of the carbamates is methanol [28]. Therefore, methanol was chosen as desorption solvent in this experiment. Ultrasonication was used as the desorption device for desorption of carbamates from the sorbent. The concept of desorption process is the same as the extraction process as the process is non-exhaustive, whereby desorption of the analytes into the solvent is based on equilibrium and adsorption back to the sorbent might occur as desorption time increased. For the FND-CHF, 10 minutes was chosen as it gave the overall highest peak areas (see Fig. 5).

3.4 Salting-out effect

The optimized salt content was investigated by extracting 50µg.L^{-1} carbamate mixture. The salt content evaluated was from 3 to 30%w/v for the sorbent. 3%w/v of salt content was chosen as the lowest salt content evaluated because the normal salt content in sea is 3%w/v.

It is normal to see the increasing amount of analyte extracted with increase of the salt content in solution during extraction. This is because the dissolved ionic salts tend to form shells of tightly-bound water, which is normally named as hydration shells. With increasing salt concentration, more and more water bound up in hydration shells. As a result, less water is available for forming cavities around target analytes. This process is called electrostriction. Thus, increase of salt content generally leads to a decrease in the solubility of hydrophobic organic solutes due to salting-out effect.

Since the largest peak areas shown in Fig. 6 for the FND-CHF are 30%w/v salt content, all the next experiments were conducted using the optimized concentration.

3.4 pH effect

The optimized pH was investigated by extracting 50µg.L^{-1} carbamate mixture (see Fig. 7). The pH evaluated was from 2 to 12 for the sorbent. The FND-CHF, pH 2 gave the highest extraction efficiency. This phenomenon might be due to the fact that when pH decreases, the carbamates protonate, creating a positively charged ionic species and can interact more with the functional group on the nanodiamond.

It was observed that at alkaline conditions, the areas for all target analytes were significantly decreased. This is referred to hydrolysis effect [29].

4. Optimal extraction conditions

After evaluation of different parameters for extraction, 30 minutes extraction time, 10 minutes desorption time, 30%w/v salt content and pH of 2; were used to assess the FND-CHF in extracting carbamate pesticides.

4.1 Method validation

In order to assess the applicability of the proposed techniqe, the optimum values of all studied extraction conditions were used in the investigation of the method's linearity, precision and limit of detection (LOD). The performance of the proposed novel method under all optimized conditions is shown in Table 1.

The external calibration plot contrived showed that all five compounds exhibited very good linearity range with correlation coefficients between 0.9909 and 0.9970. The R.S.D values ranged from 3.4 to 9.7 %. The FND-CHF are not available commercially, and were coated in the laboratory, the coating on the hollow fiber might not be consistent causing the R.S.D values to be varied. However, good limits of detection (LODs) in the range of 0.044 - 0.084 $\mu g.L^{-1}$ were obtained, based on S/N = 3.

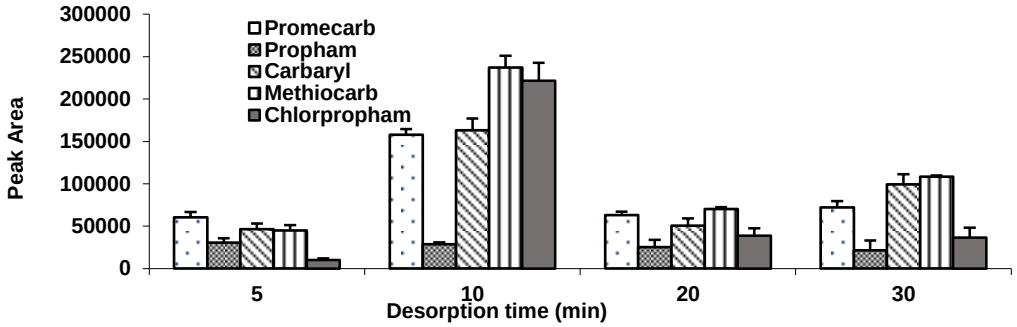


Fig. 5: The desorption time effect on the extraction efficiency for FND-CHF.

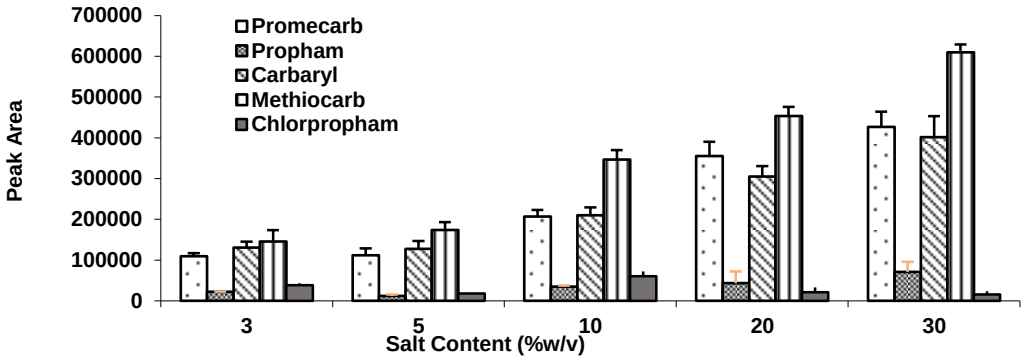


Fig. 6: The salting-out effect on the extraction efficiency for FND-CHF.

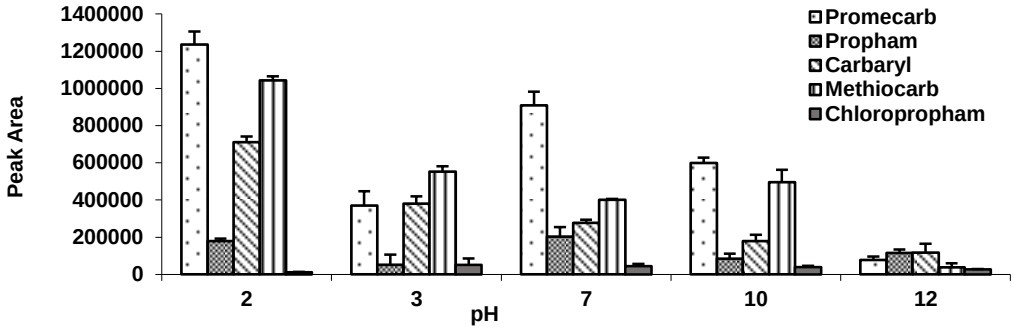


Fig. 7: The pH effect on the extraction efficiency for the FND-CHF.

Table 1: Performance of FND-CHF

Analytes	Linearity range ($\mu g.L^{-1}$)	Correlation coefficient	Reproducibility (%)	Limit of detection (($\mu g.L^{-1}$)
Promecarb	0.1-20	0.9909	3.4	0.072
Propham	0.1-20	0.9934	3.7	0.055
Carbaryl	0.1-20	0.9970	6.3	0.044
Methiocarb	0.1-20	0.9955	7.7	0.084
Chlorpropham	0.1-20	0.9944	6.3	0.065

4.2 Comparison of different methods

Comparison of the method was made based on the limit of detection (LOD). The limit of detection was evaluated by comparing the mean of the peak areas of extraction with the peak area of a standard solution. Table 2 shows the comparison of limit of detection of the novel method proposed in this project and others mentioned in published works. The LOD of LPME was taken from a published paper [21].

Table 2: Comparison of LOD obtained by FND-CHF with different extraction methods.

Methods	**Sample Type**	**Linearity Range (µg. L^{-1})**	**LODs (µg. L^{-1})**	**Extraction Time (min)**	**%RSD**	**Ref.**
MWCNTs[a]-HF-LPME-HPLC-DAD	Water	0.5-300	0.1-1	30	3.2–6.2	[10]
LPME[d]-GC-MS	Water	1-400	0.2-0.8	30	4.9 -7.8	[21]
HF-HPLC-GC-FTD	Water	0.3–100	0.074	20	10.2	[26]
LLE-LTP[b] -HPLC-UV	Water	33–10000	5–10	180	3.2–11.7	[30]
MWCNTs/DLLME [c] -HPLC-DAD	Water	5–1000	0.1–0.5	1	-	[31]
SPE[e]-GC-MS	Water	0.025-0.52	0.01	-	2-12.0	[32]
FND-CHF-GC-MS	Water	0.1-20	0.044-0.085	30	3.4- 7.7	Proposed

[a]MWCNTs : Multi-walled carbon nanotubes

[b]LLE-LTP: liquid–liquid extraction with low temperature partitioning.
[c]DLLME: Dispersive liquid-liquid microextraction
[d]LPME: Liquid phase microextraction
[e]SPE: Solid phase extraction

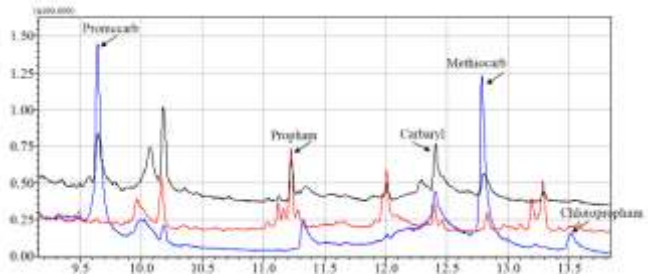


Fig. 8: GC-MS chromatograms of carbamates

Black – 500ppb standard.
Red – Hollow fiber without coating (50ppb)
Blue – Hollow fiber coated with functionalized nanodiamond in 30% salt content (50ppb)

Generally, the FND-CHF are able to achieve lower detection limit compared to the most of compared methods. Thus, novel method is preferred technique to be used in extracting carbamates from water sample. More investigation should be done on the analytes in order to achieve lower LOD using the novel extraction method.

The PDMS-coated hollow fibers without the functionalized nanodiamond were prepared to compare with the hollow fibers coated with functionalized nanodiamond. These two hollow fibers were used to extract 50µg.L^{-1} carbamate mixture. Fig. 8 shows the GC peaks for both hollow fibers with and without functionalized nanodiamond. From the chromatograms shown, the peaks of FND-CHF gave significantly higher peaks compared to the peaks given by hollow fiber coated with PDMS only. This proved that the functionalized nanodiamonds are able to increase the extraction efficiency dramatically.

5. Application to real sample

The proposed method was developed, and then applied to extract carbamate pesticides from local water. the real water samples were collected from agricultural well located at Al-Burg Village in Hebron City-Palestine.

From the experimental results, none of the target analytes were detected in the real water sample. This is because there were no extensive agricultural activities in that area for more than 10 years ago. That's why no traces of the pesticides were found. However, the proposed method can still be used in investigating water samples in other areas.

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