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Metal Organic Framework-Based Dispersive Solid-Phase Microextraction of Carbaryl from Food and Water Prior to Detection by Ultra-Performance Liquid Chromatography-Tandem Mass Spectrometry

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Abstract: In this work, metal organic frameworks (A100 Al-based MOFs) were used in dispersive solid-phase microextraction (DSPME) for the isolation and preconcentration of the carbaryl from vegetable, fruit and water samples. The A100 Al-based MOFs showed excellent behavior for the adsorption of carbaryl from a water–ethanol solution; additionally, carbaryl was easily desorbed with ethyl acetate for detection by ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-TMS). The analytical process of DSPME together with UPLC-TMS provides the accurate monitoring of trace carbaryl residues. The results show that the optimal recovery% of carbaryl was obtained at a sample apparent pH of 5, with the application of 1 mL of ethyl acetate to elute the carbaryl from the A100 Al-based MOFs. The limit of detection (LOD) and the limit of quantification (LOQ) were 0.01 mg.L^{-1} and 0.03 mg.L^{-1}, respectively. The RSD% was 0.8–1.9, and the preconcentration factor was 45. DSPME and UPLC-TMS were successfully used for the isolation and detection of carbaryl in food and water samples.

Keywords: metal organic frameworks; dispersive solid-phase microextraction (DSPME); carbaryl; ultra-performance liquid chromatography-tandem mass spectrometry; food; water

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1. Introduction

Carbaryl is a pesticide that is classified as carcinogenic to the human body [1,2]. This pesticide contaminates the environment via its extensive use to reduce flies in agriculture, and the residues of carbaryl may be adsorbed to vegetables and fruits or leached into water, leading to human exposure [3–9]. High mortality rates and low fertility were observed in rats exposed to carbaryl over three generations. Two studies in which dogs were fed carbaryl presented teratogenic effects, but were neglected because of the difference in metabolism between dogs and humans [3–5,10–12]. The permitted carbaryl limit in carrots and fruits is reported as 0.5 mg.kg^{-1} and 0.8 mg.kg^{-1}, respectively, as stated by the Codex Alimentarius, the Food and Agriculture Organization of the United Nations and the World Health Organization [13]. It is reported that the maximum acceptable carbaryl concentration (MAC) in drinking water is 0.09 mg.L^{-1}, while the acceptable daily intake (ADI) of carbaryl in drinking water has been established by the Food and Agriculture Organization (FAO) and the World Health Organization (WHO) as 0.01 mg.kg^{-1} bw/day [14].

Carbaryl may exist in environmental matrices in trace amounts, which may not be discernable by currently available detection methods. In addition, food and water samples present complex matrices and require many steps for the purification and extraction of carbaryl [15–19]. The diversity of environmental samples leads to the limitation of the

possibility of determining more than one analyte in some cases [20,21]. Many factors control component analyses, including the nature of samples and their matrix, sample preparation procedures and instrumental detection process [22–25]. Sensitive and selective analytical methods, based on mass spectrometry, were recently applied for the analysis of environmental pollutants [26–28]. Many instruments were applied for the determination of carbaryl, including high-performance liquid chromatography (HPLC) and gas chromatography (GC); however, these techniques still suffer from many limitations, such as relatively high detection limits as well as matrix interference [29,30]. The application of sample purification and extraction can solve these limitations [31,32]. Common analyte extraction procedures include solid-phase extraction, dispersive liquid–liquid microextraction, supramolecular microextraction and solid-phase microextraction [17,19,33–40]. For example, dispersive liquid–liquid microextraction coupled with HPLC-diode array detection [41] was applied as a sensitive method for the detection of different carbamates in water samples, and was reported to have RSDs of 4.7–6.5%. Goulart et al. [42] optimized and validated a liquid–liquid extraction method with low temperature partitioning for the extraction of carbaryl from chocolate milk and a grape juice sample, and used HPLC to determine the concentration of the extracted carbaryl and reported a recovery% exceeding 90%. Sharma et al. [24] validated a new spectrophotometric method to determine carbaryl in the different types of environmental samples (water, soil and foodstuffs). The method was based on methylamine coupling resulting from the microwave-assisted alkaline hydrolysis of the insecticide with CS_2 and $(CH_3COO)_2Ni$ to form a complex (nickel(II) methyl-dithiocarbamate) that was measured at 380 nm. The recovery of carbaryl from the vegetables and spiked water samples was 87.60–92.80% with RSDs of 0.54–1.02%. Paiga et al. [23] validated a liquid chromatography method for the detection and quantification of carbaryl in rat feces. The data showed a high recovery% (97.9%) and a relative standard deviation of 1.1% at 167 µg/kg.

MOFs, first introduced by Yaghi et al. [43], are porous structures constructed from the coordinative bonding between organic linkers and metal ions, with superior properties concerning their chemical and physical stability. MOFs have a high surface area, high loading capacity, nanoscale porosity, structural flexibility and unlimited diversity originating from various combinations of metals and organic parts, which enable easy manipulation through the correct selection of primary precursors and preparation conditions [44–47]. Moreover, the application of MOFs as suitable adsorbent materials has increased in separation science, including their use in solid-phase extraction [47–50]. Zhang et al. [51] synthesized nanoporous carbon (large surface area) using the MOF-ZIF-90-NPC coupled with gas chromatography-micro electron capture detection (GC-µECD) for the measurement of pyrethroid pesticides. In addition, Kahkha et al. [52] optimized the conditions for applying a zirconium-based MOF (Zr-MOF-NH_2) for the preconcentration of carbamazepine that was measured by HPLC. However, the application of MOFs for the extraction of environmental pollutants needs more investigations to evaluate the efficiency for various analytes, in case of different sample matrices for better preconcentration and purification processes prior to instrumental detection. Therefore, this work aims to develop a dispersive solid-phase microextraction (DSPME) method based on A100 Al-based MOFs as adsorbents for the isolation and preconcentration of carbaryl from vegetable, fruit and water samples. Based on our survey, this is the first time A100 Al-based MOFs have been applied for the preconcentration of carbaryl by DSPME prior to UPLC-TMS determination.

2. Experimental

2.1. Reagents and Instruments

High-purity (HPLC-grade) chemicals were used during this study. A carbaryl standard with purity 100%, A100 Al-based MOFs (commercial name: Basolite® A 100) and acetonitrile, propanol, ethyl acetate, ethanol and methanol were purchased from Sigma-Aldrich (St. Louis, MO, USA). A Milli-Q water purification system (Millipore, Bedford, MA, USA) was used to produce high-purity deionized water after filtration through a 0.45 µm

nylon filter. A solution of 10 mg.L^{-1} of carbaryl was prepared as a stock solution in a 1:2 (v/v) acetonitrile:water ratio. The working standard solutions were prepared for daily use by the dilution of the stock solution. A Waters ACQUITY ultra-performance liquid chromatography (UPLC) instrument was used for carbaryl detection; the conditions of detection as well as the calibration curve (Figure S1) are provided in the Supplementary Materials.

2.2. DSPME Preconcentration Process

For the extraction of carbaryl by DSPME before the UPLC-TMS analysis, 0.02 mg of the A100 Al-based MOFs was placed in a centrifuge tube of 50 mL volume. Then, 45 mL of carbaryl in a water/ethanol solution was added, and the solution mixture was adjusted to the apparent pH of 5 using a phosphate-buffered solution. The mixture was then shaken for 120 min, and the carbaryl was adsorbed on the MOF materials. Complete extraction was achieved by centrifuging the mixture at 1000 rpm for 10 min. The adsorbed carbaryl was then eluted with 1 mL of ethyl acetate and detected by UPLC-TMS.

The recovery was calculated using Equation (1):

$$Recovery\% = \left(\frac{C_f}{C_0}\right) * 100, \quad (1)$$

where C_f is the final concentration, and C_0 is the initial concentration.

The same steps for DSPME before UPLC-TMS analysis were performed to study the effect of apparent pH on the microextraction efficiency, eluent type and volume, sample volume optimization and matrix effect by testing the common coexisting ions. All optimization treatments were performed in triplicate with blank readings to ensure the quality of the results. Spiking for the addition recovery evaluation was operated with a standard carbaryl solution of 0.3 mg.L^{-1} (n = 3), in which 0.3 mg.L^{-1} of the carbaryl standard solution was injected in the sample mixture of 45 mL, including 2 mL of the sample extract and buffer solution at an apparent pH of 5; the recovery of the spiked solution was evaluated by considering the recovered carbaryl concentration, in this case, as the subtraction of the original carbaryl content from the final detected concentration (C_f). In addition, intra-day and inter-day analyses were performed to evaluate the precision for 0.01, 0.05 and 0.1 mg.L^{-1} of carbaryl with 7 replicates [53–57].

For the determination of carbaryl in the fruit and vegetable samples, fresh samples were collected from Riyadh city markets. The samples were washed and then cut into small pieces. Twenty grams of each fresh sample was ground in a kitchen mixer, and the final volume was adjusted to 50 mL with deionized water. The extract of the raw sample was used as a stock solution to optimize the proposed microextraction procedures. In particular, portions of 2 mL each were used for the previously described DSPME procedure. The real sample volume in the range of 1–45 mL can be subjected to the previously described DSPME procedures.

3. Results and Discussion

3.1. Optimization of the Conditions for the Preconcentration of Carbaryl

The recovery% of carbaryl after the adsorption onto A100 Al-based MOFs dispersed in a water/ethanol solution during the solid-phase microextraction process was investigated and improved. Due to the extraction mechanism, the procedure was termed DSPME. The developed microextraction procedure was optimized in terms of several controlling parameters, such as the pH, eluent type, eluent volume, sample volume and addition/recovery studies from the real samples [58]. The morphology of the A100 Al-based MOFs was examined by SEM (Figure S2A,B), which showed separated particles in the microscale structures with a crystalline nature (XRD Figure S3). The FTIR examination (Figure S4) for A100 Al-based MOFs showed surface functional groups at 1400 cm^{-1} and 1700 cm^{-1}, respectively, due to the presence of carbonyl and carboxylic groups in the terephthalate structure of the A100 Al-based MOFs. The peak detected at 3300 cm^{-1} to 3600 cm^{-1} is related to the hydroxyl groups from adsorbed water. These polar functional groups in the

adsorbent surfaces (A100 Al-based MOFs) play an important role in Van der Waals forces, the dipole–dipole interaction with carbaryl during the microextraction process. Herein, the adsorption capacity for carbaryl onto the applied MOFs is 84 mg/g.

3.1.1. Effect of the Apparent pH on Carbaryl Recovery%

In the microextraction method, the A100 Al-based MOFs act as a matrix for the adsorption/desorption of carbaryl and allows for its uptake from the sample extract as the first step of the preconcentration process. Since the apparent pH of the sample solution is a very important factor for the quantitative recovery of carbaryl in solid-phase microextraction, the influence of the apparent pH of the analyte solution on the recovery was investigated in the apparent pH range of 2.0–8.0. Figure 1 shows that at apparent pH 5 and 8, the recovery of carbaryl approaches its maxima, and there is no increase after pH 8, which indicates that carbaryl adsorption is pH-dependent; a pH of 5 was used during the subsequent optimization steps. The separation of carbaryl onto A100 Al-based MOFs depends on the electrostatic interaction between the nitrogen and oxygen atoms in the carbaryl and the active sites on the A100 Al-based MOFs, such as the carbonyl groups. It is reported that the apparent pH of the medium may affect the attraction adsorption forces during the extraction, due to protonation of carbonyl on the surfaces of A100 Al-based MOFs in an acidic medium. Furthermore, the π–π stacking is expected to share in the adsorption, attracting the forces of the aromatic rings in carbaryl and A100-Al-based MOFs.

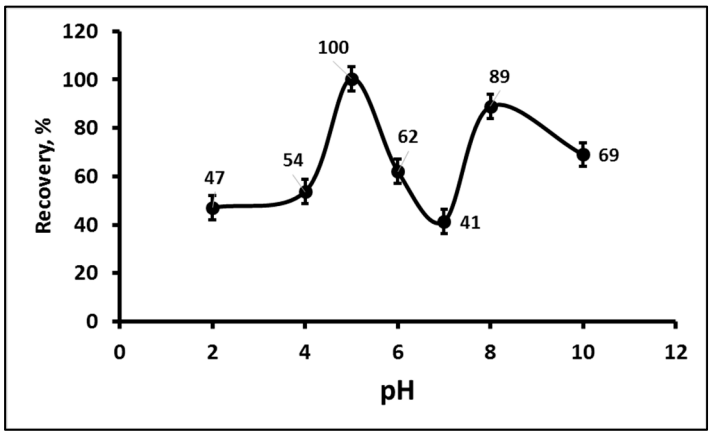


Figure 1. The effect of the apparent pH on the recovery of carbaryl from A100 Al-based MOFs (n = 3).

3.1.2. Effect of the Eluent Type on the Desorption of Carbaryl

The recovery of the adsorbed carbaryl pesticide from the A100 Al-based MOFs was studied by testing several organic solvents with different polarities. Figure 2 shows the recovery% of carbaryl when different eluents were implemented, including propanol, acetonitrile, ethyl acetate, ethanol and methanol, which were found to be 27, 82, 97, 81 and 82%, respectively. The quantitative recoveries for carbaryl were obtained with ethyl acetate. This indicated that ethyl acetate was sufficient for the desorption of carbaryl from the A100 Al-based MOFs. Ethyl acetate is reported for pesticide elution [52], which may be enhanced by the presence of carboxylic group in their structure, enabling them for a high electrostatic interaction for the dissolution and elution of analytes.

3.1.3. Effect of the Eluent Volume on Carbaryl Recovery%

To determine the lowest amount of ethyl acetate required to recover the adsorbed carbaryl from the A100 Al-based MOFs, different amounts were examined over the volume range of 1–5 mL. As shown in Figure 3, quantitative recoveries are obtained with 1 mL of ethyl acetate. To achieve a higher concentration, a lower volume of eluent was required; hence, the 1 mL volume of the ethyl acetate that yielded a good recovery was also a sufficiently small volume.

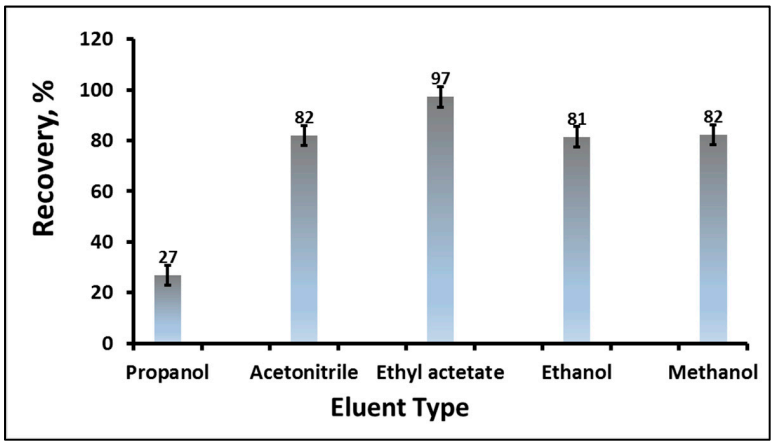


Figure 2. Effect of the eluent type on the desorption of carbaryl from A100 Al-based MOFs (n = 3).

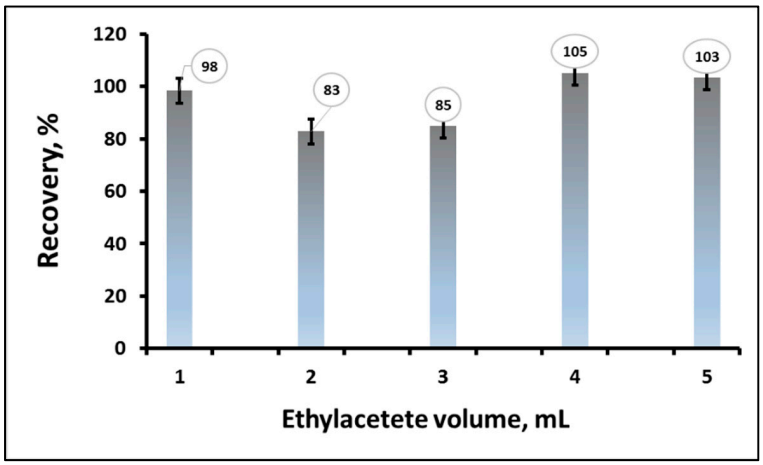


Figure 3. Effect of the eluent volume on the desorption of carbaryl from A100 Al-based MOFs (n = 3).

3.1.4. Effect of the Sample Volume on the Recovery% of Carbaryl

The starting carbaryl-containing sample volume is important during the development of the microextraction procedure, as microextraction procedures are able to recover analytes from a large sample volume, increasing the extraction efficiency and the preconcentration factor [59–61]. In this work, the sample volume was studied in the range of 10 to 50 mL. As shown in Figure 4, the quantitative recoveries obtained are up to 45 mL. By considering the eluate volume of 1 mL, the preconcentration factor was calculated as 45.

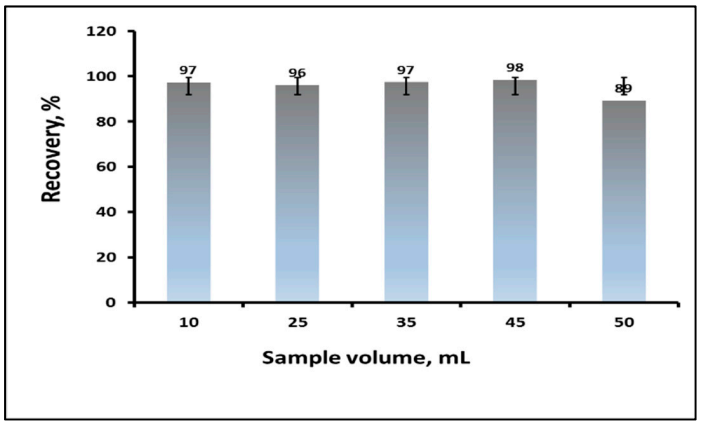


Figure 4. Effect of the sample volume on carbaryl recovery% (n = 3).

3.1.5. Effect of the Coexisting Ions on Carbaryl Recovery%

Investigations to assess the recovery% of carbaryl in presences of some species, such as common cations or anions, are conducted and the results are presented in Table 1. The recoveries are higher than 93% for all the evaluated ions. The obtained percentage recoveries are in the range of 95–100%, indicating that the proposed microextraction procedure is matrix independent.

Table 1. The recovery of carbaryl from water in the presence of coexisting ions (n = 3).

Co-Existing Ion	Carbaryl Recovery%
Ca^{2+}	97.0 ± 0.2
Mg^{2+}	99.0 ± 1.0
Ni^{2+}	98.0 ± 0.9
Fe^{2+}	96.0 ± 0.5
Zn^{2+}	96.0 ± 0.8
Na^{2+}	100.0 ± 0.2
Cl^{2+}	97.0 ± 0.5
$SO_4{}^{2-}$	99 ± 0.09
$NO_3{}^{-}$	95.0 ± 1.2

3.1.6. Analytical Features

To validate the developed analytical procedure, real samples of different kinds, including water, fruits and vegetable samples, were subjected to the developed microextraction procedure, followed by UPLC-TMS analysis for the determination of carbaryl residues. The feasibility of the proposed procedure was determined by spiking the real samples with known concentrations of carbaryl. The results are presented in Table 2 for the water, fruit and vegetable samples. A high efficiency of the DSPME procedure for carbaryl analysis was observed. A good agreement was found between the amounts of carbaryl that were added and measured; additionally, the recovery% was ≥91%. These results reveal the accuracy of the DSPME procedure and indicate that the method is matrix independent. The results show that the optimal quantitative recovery of carbaryl is obtained at apparent pH 5 with 1 mL of ethyl acetate as the eluent.

Table 2. The recovery of carbaryl from the water and food samples (n = 3).

Samples	Carbaryl Concentration	Recovered Concentration after Spiking 0.300 mg.L^{-1} Carbaryl	Recovery%
Tap water	0.00 mg.L^{-1}	0.298 ± 0.050 mg.L^{-1}	99
Apple extract	0.01 mg.kg^{-1}	0.294 ± 0.050 mg.L^{-1}	98
Tomato extract	0.02 mg.kg^{-1}	0.279 ± 0.40 mg.L^{-1}	93
Red radish	0.01 mg.kg^{-1}	0.285 ± 0.040 mg.L^{-1}	95
Mango	0.01 mg.kg^{-1}	0.292 ± 0.010 mg.L^{-1}	97
Carrot	0.01 mg.kg^{-1}	0.274 ± 0.005 mg.L^{-1}	91

The preconcentration factor (PF) was calculated from Equation (2)

$$PF = \frac{Initial\ sample\ volume}{Final\ sample\ volume} \quad (2)$$

The limit of detection (LOD) was calculated using Equation (3)

$$LODs = \frac{(3{*}\mathrm{STD})}{m} \quad (3)$$

The limit of quantification (*LOQ*) was calculated using Equation (4)

$$LOQs = \frac{(10*\mathrm{STD})}{m} \quad (4)$$

where STD is the standard deviation of seven blank readings, and m is the experimental preconcentration factor, calculated considering the ratio of the slopes of the calibration curves with and without the DSPME pre-concentration procedure, which is evaluated in the range from 0.025 mg.L^{-1} to 1.000 mg.L^{-1}.

The detection limit (*LOD*) and the quantification limit (*LOQ*) were 0.01 mg.L^{-1} and 0.03 mg.L^{-1}, respectively. The preconcentration factor was 45.

The accuracy and reproducibility of the proposed DSPME procedure were investigated by the evaluation of intra-day and inter-day precision for carbaryl by DSPME. The evaluation procedures were performed using 0.01, 0.05 and 0.1 mg.L^{-1} carbaryl solution (n = 7), as presented in Table 3. The accuracy% was reported in the range 0.2–6.6 and the calculated relative standard deviation (RSD%) was in the range of 0.27–2.13, revealing the high precision and reproducibility of the developed DSPME.

Table 3. Evaluation of the intra-day and inter-day precision for (n = 7).

Carbaryl Solution (mg.L^{-1})	Intra-Day Analysis			Inter-Day Analysis								
				First Day			Third Day			Fifth Day		
	Detected Concentration (mg.L^{-1})	Accuracy%	Precision (RSD%)	Detected Concentration (mg.L^{-1})	Accuracy%	Precision (RSD%)	Detected Concentration (mg.L^{-1})	Accuracy%	Precision (RSD%)	Detected Concentration (mg.L^{-1})	Accuracy%	Precision (RSD%)
0.01	0.010	2.0	0.87	0.010	3.5	0.85	0.010	3.8	0.27	0.011	7.2	1.03
0.05	0.050	0.2	1.05	0.051	1.2	2.13	0.049	0.6	1.68	0.051	2.2	1.72
0.10	0.104	4.1	1.4	0.107	6.6	1.9	0.106	6.0	0.8	0.104	3.7	1.7

By comparing the achieved efficiency for carbaryl microextraction using A100 Al-based MOFs with that of the other reported methods (Table 4), the DSPME procedure developed in this study exhibits a high microextraction efficiency, which enables the trace analysis of carbaryl. The proposed DSPME procedure was less sensitive than the other reported methods, such as SPE-GC [62] and DLLME-HPLC [41], while it exhibited a higher sensitivity, compared to the other procedures, including QuEChERS [63], LLE-LTP-HPLC-UV [42], QuEChERS-LC-FLD [64] and UHPLC-QqQ-MS/MS [65]. These results indicate the potential application of A100 Al-based MOFs as a solid phase for developing extraction procedures for the preconcentration of carbaryl from various environmental samples. In addition, the proposed DSPME procedures described in this work have a good sensitivity, compared with the main analytical procedures used for the quantification of carbaryl.

Table 4. Comparison of the carbaryl microextraction method developed in this study with the previously reported methods.

Method Description	Limit of Detection	Limit of Quantification	RSD	References
SPE-GC	0.05 mg.kg^{-1}	0.15 mg.kg^{-1}	4.7%	[62]
DLLME-HPLC	0.4–1.0 µg.L^{-1}	1.3 µg.L^{-1}	5.1%	[41]
QuEChERS	1.0 mg.kg^{-1}	-	4%	[63]
LLE-LTP-HPLC-UV	8.0 mg.L^{-1}	25.0 mg.L^{-1}	-	[42]
QuEChERS-LC-FLD	27.7 mg.kg^{-1}	92.3 mg.kg^{-1}	1.1%	[64]
UHPLC-QqQ-MS/MS	-	10 mg.kg^{-1}	4%	[65]
DSPME	0.01 mg.L^{-1}	0.03 mg.L^{-1}	0.27–2.13%	This work

4. Conclusions

A DSPME procedure was developed by applying A100 Al-based MOFs as adsorbents for the microextraction of carbaryl from vegetables, fruits and water. The application of DSPME in combination with ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-TMS) allowed for the high-sensitivity detection of carbaryl. The optimized conditions for the microextraction were successfully applied to sample volumes of up to 45 mL. The proposed DSPME procedure enabled a preconcentration factor of 45 and showed matrix-independent behavior. The presence of the terephthalate in the A100 Al-based MOFs enhanced the carbaryl microextraction. The developed procedure can enhance the determination of carbaryl in various food samples, which help in keeping food safety worldwide. The DSPME possesses a high sensitivity, compared with the other procedures that were applied for the extraction of carbaryl. In addition, the effective efficiency of applying metal organic frameworks for microextraction, as reported in this work, will open the space for more research and investigations for the microextraction of various categories of other environmental pollutants. The future research will focus on the improvement of MOFs structures towards the adsorption and preconcentration applications, which may include functionalization with suitable ligands and/or the variation of the metal core in the entire MOFs structure. The variation of the MOFs functional groups and properties is expected to enhance the adsorption/desorption processes of the broad range of species for micro-extraction applications, whether for environmental pollutants and/or biomolecule analysis.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/separations9020032/s1: Figure S1: calibration curve for carbaryl determination by UPLC-TMS; Figure S2: SEM (A,B) of metal organic frameworks (A100 Al-based MOFs); Figure S3: XRD of metal organic frameworks (A100 Al-based MOFs) and Figure S4: FTIR of metal organic frameworks (A100- Al-based MOFs).

Author Contributions: Formal analysis, M.A.H., B.A., M.S. (Mohamed Sheikh), A.A.G. and Z.A.A.; Funding acquisition, M.A.H.; Investigation, M.A.H., A.E.-M. and Z.A.A.; Methodology, M.A.H., B.A., M.S. (Mohamed Sheikh) and A.A.G.; Resources, Z.A.A. and M.S. (Mustafa Soylak); Supervision, M.A.H.; Validation, M.S. (Mustafa Soylak); Writing—original draft, B.A.; Writing—review and editing, M.A.H., A.E.-M., M.S. (Mohamed Sheikh), Z.A.A. and M.S. (Mustafa Soylak). All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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