Microchemical Journal 130 (2017) 64–70

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Preconcentration of carbamate insecticides in water samples by using modified stir bar with ZnS nanoparticles loaded on activated carbon and their HPLC determination: Response surface methodology

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ARTICLE INFO

Article history:
Received 8 January 2016
Received in revised form 13 June 2016
Accepted 7 August 2016
Available online 9 August 2016

Keywords:
Experimental design
HPLC
N-methylcarbamates
Stir bar sorptive extraction
Water samples

ABSTRACT

In this paper, a zinc sulphide nanoparticles loaded on activated carbon (AC) (ZnS-AC) as well as 1-ethyl-3-methylimidazolium hexafluorophosphate ([EMIM][PF_6]) ionic liquid using sol gel technique was used as the adsorbent for the stir bar sorptive extraction (SBSE) of *N*-methylcarbamates (NMCs) (carbofuran, carbaryl and promecarb) in water samples followed by high performance liquid chromatography-ultraviolet detection (HPLC-UV). The fractional factorial design (FFD) was used to find the most important factors, which were then optimized by the central composite design (CCD) and response surface methodology (RSM). At optimum conditions values of factors set as 2.75% (w/v) NaCl, 23 min extraction time, 300 μL methanol (as desorption solvent), natural pH, and 500 rpm stirring speed. Under the optimal experimental conditions, the proposed method has linear ranges over 0.002–30 μg mL^{-1} with detection limit 0.0003–0.0005 μg mL^{-1} and good RSDs (and $n = 6$) of 3.3–4.5% for NMCs. The developed method has been successfully applied to the determination of three NMCs in environmental water samples such as tap water, river water, and mineral water.

1. Introduction

Carbamate pesticides are widely applied in agricultural production [1,2] and their residues are unavoidable and harmful to environmental water and human health [3–5]. Therefore, the sensitive detection of carbamate pesticides in the environment and agricultural products is important. Generally, the carbamate residues in the environment are found at low concentrations within complex matrices, so sample pretreatment and concentration prior to instrumental analysis is one of the most crucial steps in the analytical process. Traditionally, liquid– liquid extraction (LLE) and solid phase extraction (SPE) have been used for the preparation of water samples prior to analysis [2,4]. However, these methods are typically time-consuming and tedious. In the last few years, the trends for simplifying the analytical procedures have driven to the development of new analytical approaches which enable the determination of pollutants in complex matrices. For these reasons, new extraction techniques based on various separation principles such as liquid phase microextraction (LPME), solid phase microextraction (SPME) and dispersive liquid–liquid microextraction (DLLME) have been developed and have garnered much attention [2,6–9].

In this regard, the stir bar sorptive extraction (SBSE) technique, first described in the nineties by Baltussen et al. [10], is a relatively novel and efficient technique for the extraction and concentration of organic compounds from environmental, food and biological samples using a thick film of polydimethylsiloxane (PDMS) [11,12]. Since SBSE is an equilibrium process, the analyte is extracted by partitioning between the liquid phase and the PDMS phase according to its distribution constant. For this reason, the extractant material due to its polarity, adsorption capacity, selectivity, and extraction efficiency has an important role in the SBSE method. Therefore, the preparation of novel coating materials is still one of the most important research subjects in SBSE. Conventional techniques such as sol-gel technology and monolithic materials have been applied for the modification of the coating surfaces of the stir bars [13,14]. The sol-gel technology with the advantages of high thermal stability, strong adhesion of the coating and bed, high flexibility and possibility of obtaining the coating with high surface areas is the preferred one [15,16].

In recent years, various nanoparticles have been adopted as the sorbents in SPE because of their specific properties such as excellent mechanical, thermal, high specific surface area adsorbent capacity [17,

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http://dx.doi.org/10.1016/j.microc.2016.08.002

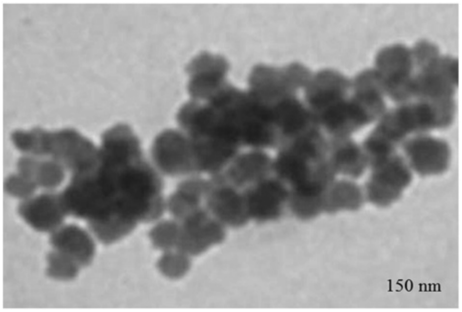

Fig. 1. The TEM image of the ZnS-AC.

18]. In this work, zinc sulphide nanoparticles (ZnS-NPs) loaded on activated carbon (AC) (ZnS-AC) were introduced as the coating materials for SBSE. The sol-gel technique was used to modify the surface of the stir bar with ZnS-AC and 1-ethyl-3-methylimidazolium hexafluorophosphate ([EMIM][PF_6]) ionic liquid. The modified stir bar with nanoparticles was then applied for the extraction and preconcentration of N-methylcarbamates (NMCs) at trace levels from water samples prior to their determination by high performance liquid chromatography (HPLC). The influence of the important factors affecting the SBSE such as pH of sample solution, ionic strength, extraction time, volume of desorption solvent, desorption time and the stirring speed was investigated and optimized by the experimental design using the two-step chemometric procedure of fractional factorial design (FFD) and the central composite design (CCD).

2. Experimental

2.1. Reagents and materials

Tetraethyl orthosilicate (TEOS), acetonitrile, acetone methanol, ethanol, dichloromethane, hydrochloric acid, acetic acid, sodium hydroxide, zinc acetate, nickel acetate, thioacetamide, Na_2EDTA and 1-ethyl-3-methylimidazolium hexafluorophosphate ([EMIM][PF_6]) were purchased from the Merck Company (Darmstadt, Germany). *N*-methylcarbamates (NMCs) insecticide standard (carbofuran, carbaryl and promecarb) were purchased from Sigma-Aldrich (Steinheim, Germany). The stock solution (200 mg L^{-1}) of carbamate insecticides were prepared by dissolving each of them in methanol and stored at 4 °C before use. The working solutions were freshly prepared through the appropriate dilution of the stock solution with double distilled/deionized water (produced by a Milli-Q system (Millipore, Bedford, MA, USA)).

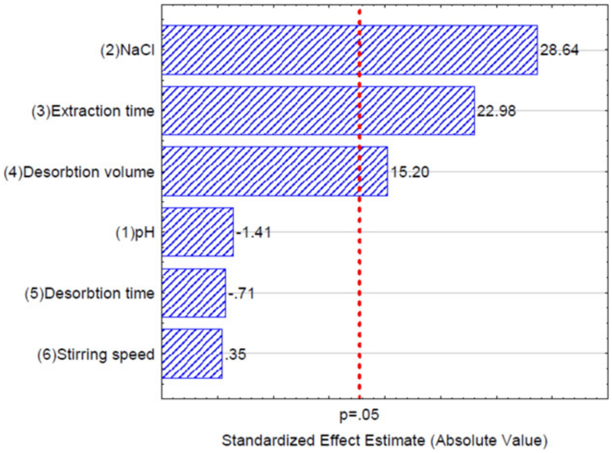

Fig. 2. Standardized main effect Pareto chart for the FFD of screening experiment. Vertical line in the chart defines 95% confidence level.

2.2. Instrumentation and software

The experimental runs for the separation and determination of NMCs were performed using a KNAUER Smart line HPLC system equipped with UV–VIS Detector (2550: was set at 220 nm), micro vacuum degasser, LPG system and a C_{18} column (250 × 4.0 mm, 5 μm) from Waters (Milford, MA, USA). The EZChrom Elite software was used to process the chromatographic data. Determination of NMCs was performed at the optimum separation condition by HPLC with isocratic

Table 1
Factors, symbols and levels in 2^{6-2} FFD design matrix.

Factors	Levels		
	Low (−1)	Center point (0)	High (+1)
(X_1) pH of sample solution	2	5	8
(X_2) Ionic strength (NaCl % (w/v))	0.0	2.5	5
(X_3) Extraction time (min)	5	15	25
(X_4) Volume of desorption solvent (μL)	100	250	400
(X_5) Desorption time (min)	5	10	15
(X_6) Stirring speed (rpm)	300	500	700

Run	X_1	X_2	X_3	X_4	X_5	X_6	ER%
1	2.0	0.0	5.0	100.0	5.0	300	46.0
2	8.0	0.0	5.0	100.0	15.0	300	37.0
3	2.0	5.0	5.0	100.0	15.0	700	76.0
4	8.0	5.0	5.0	100.0	5.0	700	63.0
5	2.0	0.0	25.0	100.0	15.0	700	54.0
6	8.0	0.0	25.0	100.0	5.0	700	58.0
7	2.0	5.0	25.0	100.0	5.0	300	70.0
8	8.0	5.0	25.0	100.0	15.0	300	83.0
9	2.0	0.0	5.0	400.0	5.0	700	60.0
10	8.0	0.0	5.0	400.0	15.0	700	42.0
11	2.0	5.0	5.0	400.0	15.0	300	65.0
12	8.0	5.0	5.0	400.0	5.0	300	74.0
13	2.0	0.0	25.0	400.0	15.0	300	78.0
14	8.0	0.0	25.0	400.0	5.0	300	74.0
15	2.0	5.0	25.0	400.0	5.0	700	85.0
16	8.0	5.0	25.0	400.0	15.0	700	93.0
17(C)	5.0	2.5	15.0	250.0	10.0	500	88.0
18(C)	5.0	2.5	15.0	250.0	10.0	500	87.0

C: center point.

Table 2
Design matrix for the 2^3 central composite designs.

Factors	Levels			Star point α = 1.682	
	Low (−1)	Central (0)	High (+1)	−α	+α
(X_1) Ionic strength (NaCl % (w/v))	1.5	2.5	4.0	0.0	5.0
(X_2) Extraction time (min)	12	18	24	8	28
(X_3) Volume of desorption solvent (μL)	150	250	350	82	418

Runs	X_1	X_2	X_3	ER%
1	1.5	12	150	38.7
2	1.5	12	350	58.4
3	1.5	24	150	65.4
4	1.5	24	350	80.5
5	4.0	12	150	53.2
6	4.0	12	350	82.6
7	4.0	24	150	73.8
8	4.0	24	350	92.5
9	0.0	18	250	58.9
10	5.0	18	250	78.5
11	2.5	8	250	52.3
12	2.5	28	250	89.6
13	2.5	18	82	43.5
14	2.5	18	418	86.5
15(C)	2.5	18	250	87.4
16(C)	2.5	18	250	86.8

C: center point.