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Dispersive nano solid material-ultrasound assisted microextraction as a novel method for extraction and determination of bendiocarb and promecarb: Response surface methodology

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ABSTRACT

A new extraction method, based on Dispersive Nano-Solid material-Ultrasound Assisted Micro-Extraction (DNSUAME), was used for the preconcentration of the bendiocarb and promecarb pesticides in the water samples prior to high performance liquid chromatography (HPLC). The properties of NiZnS nanomaterial loaded on activated carbon (NiZnS-AC) are characterized by FT-IR, TEM, and BET. This novel nanomaterial showed great adsorptive ability towards the bendiocarb and promecarb pesticides. The effective variables such as the amount of adsorbent (mg: NiZnS-AC), the pH and ionic strength of sample solution, the vortex and ultrasonic time (min), the ultrasonic temperature (°C), and desorption volume (mL) are investigated by screening 2^{7-4} experiments of Plackett–Burman (PB) design. The important variables optimized by using a central composite design (CCD) were combined by a desirability function (DF). At optimum conditions, the method has linear response over 0.0033–10 μg mL^{-1} with detection limit between 0.0010 and 0.0015 μg mL^{-1} with relative standard deviations (RSDs) less than 5.5% ($n=3$). The method has been successfully applied for the determination of the bendiocarb and promecarb pesticides in the water samples.

1. Introduction

Carbamates are one of the important classes of the pesticides used as insecticides and fungicides in the early 1950s, and nowadays are widely used in agriculture due to their broad biological activity, low bioaccumulation potentials, and relatively low mammalian toxicities. However, the carbamates affect the nervous system by disrupting an enzyme that regulates acetylcholine, a neurotransmitter [1]. These compounds are considered dangerous to the environment and human health. They are on the priority of the list released by the United States Environmental Protection Agency (EPA) [2]. The maximum residue limit (MRL) of individual carbamates was permitted by the European authorities for the quality of water intended for human consumption and for the protection of groundwater the pollution of which [3] is 100 ng L^{-1}. Consequently, it is necessary to use the highly sensitive analytical methods to recognize ultratrace levels of these compounds.

High performance liquid chromatography (HPLC) methods have been usually applied for the determination of carbamates in waters by using fluorescence [4], UV [5–7] and mass spectrometry (MS) detection [8–11]. The previous studies concerning the analysis of these compounds in water can be found in the section of literature review [12,13]. Post-column hydrolysis of N-methylcarbamates (NMCs) to methylamine (MA) and subsequent derivatisation with o-phtalaldehyde (OPA) are the basis of the HPLC-fluorescence method which has been accepted as a standard protocol by several official organizations, including EPA [14]. Chemiluminescence, a less usual detection technique in HPLC, has also been used for determination of carbamate pesticides [15,16].

Different pretreatment methods, including Liquid–Liquid Extraction (LLE) [17], Solid-Phase Extraction (SPE) [18], Supercritical Fluid Extraction (SFE) [19,20], Microwave Assisted Extraction (MAE) [21,22], Solid-Phase Micro-Extraction (SPME) [23,24] Liquid-Phase Micro-Extraction (LPME) [25–27], Single Drop Micro-Extraction (SDME) [28], and Magnetic Solid Phase Micro-Extraction (MSPE) [29] have been used for the preconcentration and cleanup of the carbamate pesticide residues from different samples prior to the instrumental analysis. LLE and SPE, as the most commonly techniques, suffer from such disadvantages as time consuming, high cost, and the need for large volumes of samples and toxic organic solvents. On the other hand, regardless of low consumption of organic solvents, SPE technique is boring, relatively expensive, and analytic breakthrough when large volumes of sample are analyzed. SPME and LPME are simple and fast, miniaturize the pretreatment processes of sample and minimize the use of organic solvents. However, these techniques suffer from some drawbacks such as sample carry-over, relatively high cost, fiber fragility, and relatively low accuracy [30,31]. More recently, a relatively new mode of LPME, the Dispersive Liquid–Liquidmicro-Extraction

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(DLLME), has been developed [32–34]. The advantages of the DLLME method include rapidity, low cost, simplicity of operation, and the high preconcentration factor. However, to enhance the dispersion of the extraction solvent in the aqueous sample phase, the use of a water-miscible organic dispersive solvent is required in DLLME, although its use could decrease the partition coefficient of analyses into the extraction solvent. However, poor detection limits, usage of dispersive solvents and toxic chlorinated solvents as extraction solvents which is non environment-friendly, are the disadvantages of this method.

Sonochemistry is an ongoing area in science and technology. The effects of ultrasound made on chemical and physical transformations are through the phenomenon of cavitation. Cavitation is the production of micro-bubbles in a liquid when a large negative pressure is applied to it [35]. Sonication can be used to produce the very fine emulsions from immiscible liquids, which result in the very large interfacial contact areas between the liquids and a corresponding dramatic increase in the mass transfer between the two immiscible phases. This leads to an increase in the extraction efficiency of the procedure in a minimum time [36,37]. For these reasons, ultrasound-assisted emulsification microextraction (USAEME) has been developed [38]. Ultrasound can be considered a useful alternative for solid sample pretreatment because the energy imparted facilitates and accelerates some steps, such as dissolution, fusion, and leaching among others [39,40]. In this method, the extractant is dispersed into the aqueous solution without any dispersant under ultrasound irradiation. Therefore, the use of toxic organic solvents is greatly reduced. The surfactants have high boiling point and are not evaporated in room temperature. Therefore, USAEME method suffers from interference of the surfactant transfer in the final extraction. In recent years, due to unique properties of Nanomaterial such as excellent mechanical, electrical, thermal, optical properties, a high adsorbent capacity and a very high specific surface area which used nanomaterial have been developed. In this study, we used NiZnS nanoparticles, loaded on activated carbon (AC) (NiZnS-AC), as the new adsorbent for extraction of carbamate pesticides (bendiocarb and promecarb) in aqueous media. In this method, nanoparticles are dispersed in aqueous media by vortex and ultrasonic device for adsorption target analyte, then adsorbed analyte is eluted and determined by HPLC–UV. Dispersive Nano-Solid material-Ultrasound Assisted Micro-Extraction (DNSUAME) as a novel method has advantages such as simple operation, fast, high sensitivity, and high linear range for determination of carbamate pesticides. The effects of various experimental parameters, such as the amount of nanomaterial, the vortex and ultrasound time, the ultrasonic temperature, the ionic strength, the pH of aqueous media and, the kind and volume of the elution solvent were investigated and optimized. In a time when approaching each other, every related single variable is varied, whilst all other variables are kept fixed at a specific set of conditions. However, this procedure requires a high number of experiments and it is also time consuming. A structured experiment design that could simultaneously take into account several variables seems to be a more convenient approach searching for the optimal operational conditions in reasonable experiments [41]. For these reasons, the response surface methodology (RSM) was used for studying the effective variables on this new method.

2. Experimental

2.1. Reagents and materials

Bendiocarb and promecarb insecticide standards were purchased from Sigma-Aldrich (Steinheim, Germany). The stock solutions (200 mg L^{-1}) of bendiocarb and promecarb were prepared by dissolving them into methanol. The working solutions were prepared by appropriate dilution of the stock solutions with double distilled water. Double distilled deionized water was used throughout the experiments, which was produced by a Milli-Q system (Millipore, Bedford, MA, USA). Methanol, acetone, acetonitrile (HPLC-grade), and sodium chloride (99%) were purchased from Merck (Darmstadt, Germany). All of the standard solutions were stored at 4 °C and brought to ambient temperature just prior to use.

2.2. Equipment and software

The chromatographic measurements were carried out with an Agilent Technologies (Wilmington, DE, USA) 1100 HPLC system equipped with Micro Vacuum Degasser (model G1379A), Quaternary Pump (model G1311A), Series Multiple Wavelength Detector (model G13658: was set at 220 nm), and a Zorbax SB-C18 (150 mm × 4.6 mm, 5 μm) (Agilent) column. The chromatographic calculations were performed using a Chemstation data handling system. Determination of bendiocarb and promecarb were performed with the condition of the optimal separation by HPLC with isocratic binary mobile phase consisting of acetonitrile:water (60:40, v/v) with flow rate of 1 mL min^{-1}. A digital pH meter (InoLab pH 730,Germany) was employed for adjusting PH. Ultrasonic device (TECNO-GAZ, 60 Hz, 130 W, parma, Italy) is equipped with digital timer and temperature controller.

The NiZnS-AC nanoparticles were characterized by BET, TEM, and FT-IR. The BET (Brunauer, Emmett, and Teller) surface areas of the adsorbent materials were measured using TriStar II 3020 (Micromeritics Instrument Corporation) surface area analyzer where N_2 gas was used as adsorbate. The morphology and dimensions of the adsorbent were determined by TEM (Transmission Electron Microscopy). Fourier transform infrared spectroscopy of the adsorbent was done by using an FT-IR spectrophotometer (Model: FT-IR JASCO 460 Plus). Spectra obtained in the range of 400–4000 cm^{-1} were analyzed.

The STATISTICA, a statistical package software version 7.0 (Stat Soft Inc., Tulsa, USA) was used for experimental design analysis and subsequent regression analysis of the experimental data. Statistical analysis of the model was performed to evaluate the analysis of variance (ANOVA). The quality of the polynomial model equation was judged statistically by the coefficient of determination R^2, and its statistical significance was determined by an *F*-test. *P*-values less than 0.05 were considered to be statistically significant.

2.3. Sample preparation

To evaluate the accuracy and applicability of the proposed method, the extraction and determination of bendiocarb and promecarb were performed in different water samples (river, tap and mineral waters). River water sample was taken from different field areas of Beshar River at Yasouj, Iran (February 2013). Also tap and mineral water samples were taken from our laboratory and local supermarket in Yasouj, Iran, respectively. The collected water samples were filtered through a 0.45 μm micropore membrane and were maintained in glass containers, then stored at a temperature of 4 °C until their analysis time.

2.4. DNSUAME procedure

Scheme 1 displays the steps followed to extract the bendiocarb and promecarb from aqueous samples: Firstly, 15.5 mg of NiZnS-AC was added to 3.0 mL end cap glass pipette tip that contained 0.1 μg mL^{-1} of bendiocarb and promecarb. To completely adsorb the analytes, the mixture was placed on a vortex assisted platform and was allowed to disperse the NiZnS-AC nanoparticles in aqueous media for 5.5 min. Then, in order to complete extraction of bendiocarb and promecarb, glass pipette tip was placed in ultrasonic bath for 5.5 min. This glass pipette tip was inverted and its contents were decanted from narrow

side to another glass pipette tip that its narrow side was closed by three layer handmade filter. This new glass pipette tip was attached to the vacuum test tube and led to the separation liquid phase from NiZnS-AC nanoparticles solid phase by vacuum pump. In the next step, the adsorb analytes was elutes by 1.0 mL acetone as desorption solvent. Desorption solvents were transformed from arm side of test tube to 1.5 mL HPLC vial. After evaporated acetone by mild nitrogen stream, the sediment phase was dissolve into 25 μL methanol and 10 μL was injected into the HPLC–UV system for analysis. A schematic of the extraction process is shown in Scheme 1.

2.5. Calculating the preconcentration factor and extraction recovery

In order to obtain the optimized extraction condition, the Extraction Recovery (ER) was used to evaluate the optimum condition. *ER%* was defined as the percentage of the total analyte (n_0) extracted into the sediment phase (n_{sed}). Consequently, calculation of the ER, as analytical response, was carried out using the following equation:

$$ER\% = n_{sed}/n_0 \times 100 = C_{sed} \times V_{sed}/C_0 \times V_0 \times 100 \quad (1)$$

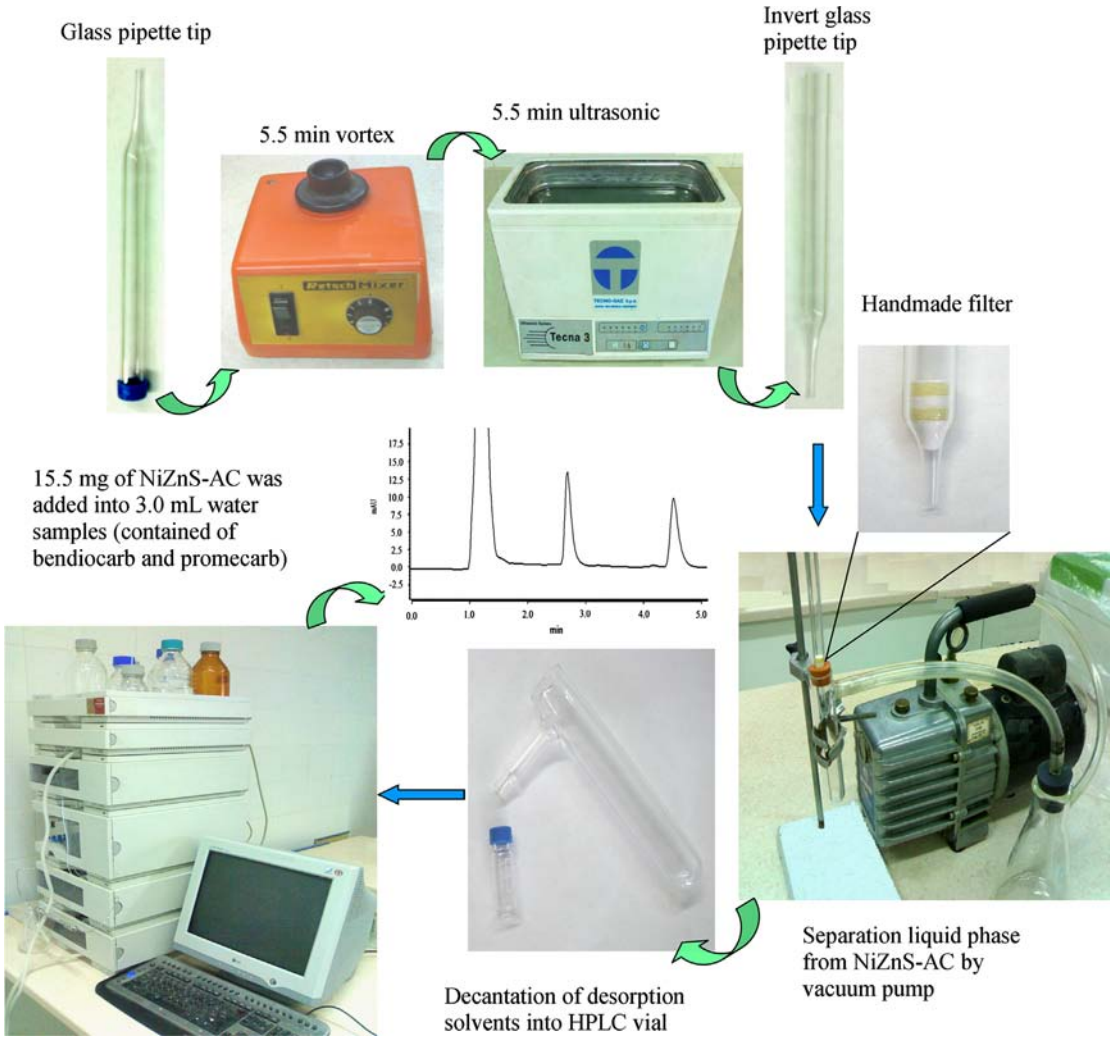
where C_{sed} and C_0 are the concentrations of the bendiocarb and promecarb in sediment phase and in aqueous sample, respectively. C_{sed} is determined from a calibration curve which was obtained using direct injection of standard solutions. V_{sed} and V_0 are the volumes of sediment phase and aqueous sample, respectively.

The preconcentration factor (PF) was defined as the ratio between the analyte concentration in the sediment phase (C_{sed}) and the initial concentration of analyte (C_0) in the aqueous sample, as follows:

$$PF = C_{sed}/C_0 \quad (2)$$

2.6. Experimental design

The experimental design was developed to decrease the number of experimental runs, and simultaneously, consider the interaction of variables to realize true optimum points with reasonable runs [42]. An experimental Plackett–Burman (P–B) design was built for the screening of the main variables affecting the ER of bendiocarb and promecarb. The methodology of P–B design is a powerful and practical tool in rapidly searching key variables from a multivariable system. This method does not determine the exact quantity, but it can provide some important information about each variable by relatively few experiments [43]. As shown in Table 1, a 2^{7-4} P–B design was applied for eight trials to estimate the significance of seven variables. The design also consists of two central points in order to estimate the experimental error (pure error) [44]. Then, the obtained effective variable on the efficiency of DNSUAME procedure were optimized by using a central composite design (CCD) and a quadratic model was built between the dependent and the independent variables.



Scheme 1. A schematic diagram of the extraction process.

Table 1
Factors, codes, low and high levels in 2^{7-4} Plackett–Burman design matrix.

Factors	Levels		
	Low (−1)	Center point (0)	High (+1)
(X_1) Adsorbent (mg: NiZnS-AC)	5.0	10.0	15.0
(X_2) pH of sample solution	3.0	7.0	11.0
(X_3) Ionic strength (NaCl % (w/v))	2.0	5.0	8.0
(X_4) Vortex time (min)	2.0	4.0	6.0
(X_5) Ultrasonic time (min)	1.5	3.0	4.5
(X_6) Ultrasonic temperature (°C)	20.0	30.0	40.0
(X_7) Desorption volume (mL)	0.5	1.0	1.5

Run	X_1	X_2	X_3	X_4	X_5	X_6	X_7	ER%
1	−1	−1	−1	+1	+1	+1	−1	57.73
2	+1	−1	−1	−1	−1	+1	+1	70.97
3	−1	+1	−1	−1	+1	−1	+1	53.36
4	+1	+1	−1	+1	−1	−1	−1	70.29
5	−1	−1	+1	+1	−1	−1	+1	54.43
6	+1	−1	+1	−1	+1	−1	−1	70.02
7	−1	+1	+1	−1	−1	+1	−1	40.64
8	+1	+1	+1	+1	+1	+1	+1	77.13
9 (C)	0	0	0	0	0	0	0	64.79
10 (C)	0	0	0	0	0	0	0	65.54

C: center point.

The CCD is one of the most frequent designs used to fit quadratic models and was first described by Box and Wilson [45]. A CCD combines a two-level factorial design with axial points (star points) and at least one point at the center of the experimental region to fit quadratic polynomials. The central points are usually repeated to get a good estimation of experimental error (pure error). The value of "*a*" is needed to ensure that the orthogonality and rotatability can be calculated from the following equation [46].

$$a = \sqrt[4]{2^f} \tag{3}$$

The total number of design points needed (N) is determined by the following equation:

$$N = 2^f + 2f + N_0 \tag{4}$$

where f is the number of variables [47], 2^f is the number of factorial points, $2f$ is the number of axial points (star point) and N_o is the number central points ($N_o = 2$). Therefore, totally 16 experiments had to be run for the CCD. The factor levels and the design matrix with the respect responses are shown in Table 2. The complete design was performed randomly in order to minimize the effect of non-controlled variables. This design is approximately able to estimate the main effects, interaction effects, and quadratic effects. A 3-factor with 5-level design is suitable for exploring quadratic response surface and constructing second-order polynomial model, widely used in RSM benefited from the following advantages:

(1) The second-order model is very flexible and can take on a wide variety of functional forms to obtain approximately the true response surface.
(2) It is easy to estimate the parameters in the second-order model using least squares method.
(3) There is considerable practical experience indicating that second-order models work well in solving real response surface problems.

When several responses were evaluated in an experimental design, the optimal points reaching individually for each factor did not coincide in all cases. There are many statistical methods for solving multiple response problems such as overlaying the contours plot for each response, constrained optimization problems, and the desirability approach. The Derringer Function (DF) [48] is the most important and the most currently used multi-criteria methodology in the optimization of analytical procedures. DF involves the transformation of each predicted response to a dimensionless partial DF d_i. The scale of the DF ranges between $d = 0$ (complete undesirable response) to $d = 1$ for a fully desired response above which further improvements would have no importance. With the individual desirability, it is then possible to obtain the overall desirability (D). The D is defined as the weighted geometric average of the individual desirability (d_i).

$$D = \left(\prod_{i=1}^{n} d_i\right)^{1/n} \tag{5}$$

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

Factors	Levels			Star point $\alpha = 1.682$	
	Low (−1)	Central(0)	High(+1)	$-\alpha$	$+\alpha$
(X_1) Adsorbent NiZnS-AC (mg)	7.0	12.0	17.0	3.6	20.4
(X_2) Vortex time (min)	3.0	5.0	7.0	1.6	8.4
(X_3) Ultrasonic time (min)	3.0	5.0	7.0	1.6	8.4

Runs	X_1	X_2	X_3	ER%
1	−1	−1	−1	56.87
2	−1	−1	1	76.69
3	−1	1	−1	67.24
4	−1	1	1	80.87
5	1	−1	−1	87.46
6	1	−1	1	82.81
7	1	1	−1	91.73
8	1	1	1	89.68
9	−1.682	0	0	58.85
10	1.682	0	0	95.45
11	0	−1.682	0	70.54
12	0	1.682	0	87.25
13	0	0	−1.682	75.15
14	0	0	1.682	93.62
15(c)	0	0	0	90.94
16(c)	0	0	0	89.81

C: center point.

where d_i indicates the desirability of the response and n is the number of responses in the measure.

3. Results and discussion

3.1. Characterization of NiZnS-AC nanoparticles

NiZnS-AC nanoparticles were synthesized in our laboratory based on the reaction of the mixture of zinc acetate [$Zn(CH_3COO)_2.2H_2O$] and nickel acetate [$Ni(CH_3COO)_2.2H_2O$] with thioacetamide (CH_3CSNH_2) in aqueous media and AC. The functional groups responsible for analyte adsorption were investigated by FT-IR analysis of NiZnS-AC. The spectra (Fig. 1a) display a number of absorption around 3436 cm^{-1} indicative of the existence of bonded hydroxyl groups. The peaks observed at 2923 and 2852 cm^{-1} can be assigned to the C–H group. The peak observed at 1631 cm^{-1} is due to C=O, and the peak at 1605 cm^{-1} that can be attributed to the aromatic C=C bond. The peak around 1118 cm^{-1} is due to C–O, and two peaks around 600–700 cm^{-1} can be assigned to the metals (Ni and Zn) attached to O and S atoms.

Fig. 1b shows the typical TEM image of the NiZnS-AC. Some surface properties and its pore size and volume were studied by surface area (BET) analysis and summarized in Table 3. The porosity and surface area of the NiZnS-AC show high surface area (1012.75 $m^2\,g^{-1}$), that may be attributed to activated carbon and presence of low sized NiZnS nanoparticles. This novel adsorbent has higher surface properties in comparison to the commercial activated carbon (122.30 $m^2\,g^{-1}$) as a standard material. The single adsorption point of total pore volume is less than 1122.517 Å width, at p/p° was around 0.552 $cm^3\,g^{-1}$, and the t-Plot micropore volume is 0.214 $cm^3\,g^{-1}$ and the BJH adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å width was 0.155 $cm^3\,g^{-1}$, while the BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å width were 0.162 $cm^3\,g^{-1}$. All these values show the ability of diffusion of analyte molecules with a size lower than these values for pore diffusion. The high surface area and porous structure of adsorbent, led to transfer target analyte from bulk solution to adsorbent surface. According to BET analysis the average size of the particles of proposed adsorbent was around 59.24 Å.

3.2. Selection of elution solvent

Before transmission of P–B design, preliminary experiments were undertaken to select the best elution solvent. To this end, DNSUAME method was applied for extraction of 0.025 μg mL^{-1} of bendiocarb and promecarb from 3.0 mL aqueous media. In this stage, desorption of bendiocarb and promecarb from NiZnS-AC nanoparticles was studied by means of 1.0 mL of different organic solvents (acetonitrile, acetone and methanol). After evaporated process of these solvents by mild nitrogen stream, the sediment phase was dissolved into 25 μL methanol and 10 μL was injected into the HPLC–UV system for subsequent analysis. It was found that among the three used solvents, the maximum sensitivity was obtained using acetone as desorption solvents for eluting adsorb bendiocarb and promecarb from NiZnS-AC nanoparticles. Therefore, acetone was chosen for subsequent experiments and the typical HPLC chromatogram of extracted bendiocarb and promecarb from distilled water was shown in Fig. 2. The effect of the volume of desorption solution on desorption efficiency of the analytes was also investigated by subsequent experimental design.

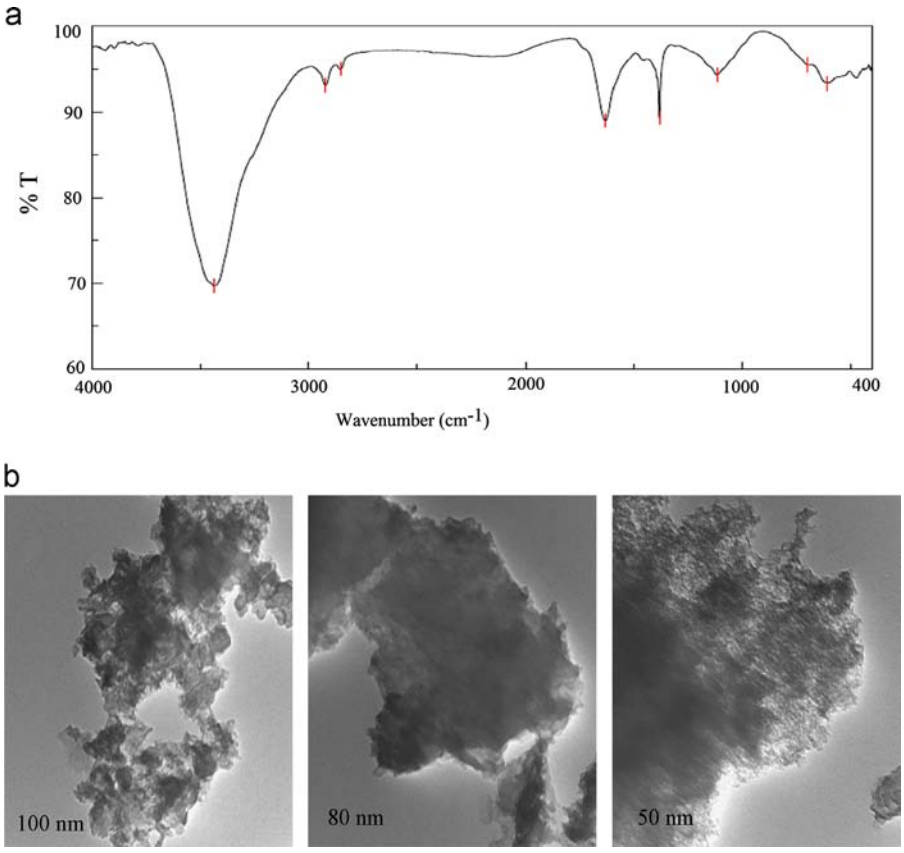


Fig. 1. (a) FT-IR spectra of NiZnS-AC and (b) TEM image of NiZnS-AC.

Table 3
Properties of NiZnS-AC obtained from BET data.

Properties of NiZnS-AC	Surface area	Single point surface area at p/p°	1009.485 $m^2 g^{-1}$
		BET Surface Area	1012.752 $m^2 g^{-1}$
		Langmuir Surface Area	1380.726 $m^2 g^{-1}$
		t-Plot Micropore Area	476.042 $m^2 g^{-1}$
		t-Plot External Surface Area	536.710 $m^2 g^{-1}$
		BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width	133.041 $m^2 g^{-1}$
		BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width	157.046 $m^2 g^{-1}$
	Pore volume	Single point adsorption total pore volume of pores less than 1190.518 Å width at p/p°	0.552 $cm^3 g^{-1}$
		t-Plot micropore volume	0.214 $cm^3 g^{-1}$
		BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å width	0.155 $cm^3 g^{-1}$
		BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å width	0.162 $cm^3 g^{-1}$
	Pore size	Adsorption average pore width (4 V/A by BET)	21.798 Å
		BJH Adsorption average pore width (4 V/A)	46.510 Å
		BJH Desorption average pore width (4 V/A)	41.292 Å
	Nanoparticles Size	Average Particle Size	59.245 Å

3.3. Plackett–Burman design (P–B)

The factorial design P–B was chosen to screen the relative effective variables on the ER of the proposed method. The effects of the seven selected variables were studied in 8 runs with the two central points that are shown in Table 1. The experiments were carried out in duplication and the mean of each run was considered. The analysis of these results produced the standardized main effect Pareto charts (P=95%) that are shown in Fig. 3. The bar length is proportional to the significance of the variables for ER%. The result indicates that the amount of adsorbent (NiZnS-AC), the vortex and ultrasonic time were the most significant variables with a positive effect on the ER% and were evaluated in the CCD for further assessment. The Ionic strength, the pH of sample solution and the ultrasonic temperature had no significant effect on the ER % and thus were eliminated for further studies. Since the effect of desorption volume, acetone, with other variables was negligible (Second-order effect combined Pareto charts in the P–B design), the value of this variable was fixed at middle level (1.0 mL) for further experiments.

3.4. Central composite design (CCD)

In the CCD, random experiments were conducted to minimize the effect of uncontrolled variables and the respective design matrix is shown in Table 2. RSM was used to investigate the influence of the three selected variables on the ER of bendiocarb and promecarb from the water samples. The main factors investigated in the present work by CCD for the improvement of ER including: the amount of NiZnS-AC nanoparticles (g, X_1), the vortex time (min, X_2) and the ultrasonic time (min, X_3). The coded values of the experimental factors and their levels for the CCD are shown in Table 2.

Table 4 presents the results of the analysis of variance (ANOVA) and regression coefficients, which suggest that the contribution of the quadratic model was significant with $p<0.05$. The lack of fit (LOF) is the variation of the data around the fitted model. LOF is a special investigative test for adequacy of a model fit, because the effects of the additional higher-order terms are removed from the error. If the model does not fit the data well, this will be significant. As shown in Table 4, a P-value of LOF was 0.188, indicating that the model fits the response well. The quality of the fit of the polynomial model equation was explained by the coefficient of determination (R^2=0. 0.977 and adjusted R^2=0.943). R^2 is a measure of the amount of deviation around the mean explained by the model. The large adjusted R^2 values indicate a good relationship between the experimental data and the fitted model. The analysis of the obtained results, by regression analysis of CCD, is shown in Table 5, and makes

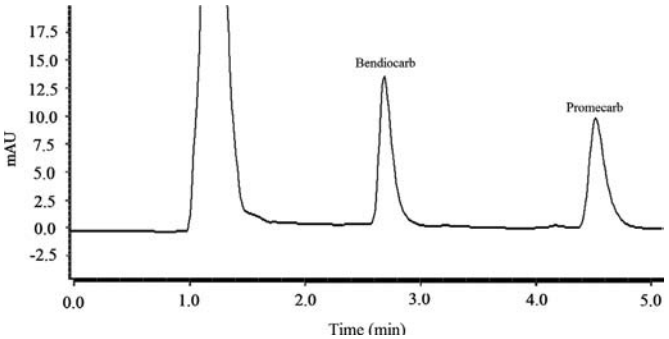


Fig. 2. HPLC chromatogram of extraction of standards solution of bendiocarb and promecarb (0.025 μg mL^{-1}).

it possible to obtain the following equation:

$$ER\% = 90.409 + 9.637X_1 + 3.939X_2 + 4.233X_3 - 4.766X_1^2 - 4.138X_2^2 - 5.018X_1X_3 \quad (6)$$

The good and successful solving of this equation, according to the desirability function (DF), makes it possible to improve the performance of the proposed method for completing and selecting the extraction of bendiocarb and promecarb and its accurate subsequent determination.

The model is applicable for prediction of the extraction amount of bendiocarb and promecarb with minimum amount of experiments. The plot of the predicted versus the observed response (ER%) and the plot of the residuals versus the predicted response of ER% are shown in Fig. 4a and b. Close inspection of Fig. 4a reveals that the residuals generally fall on a straight line which indicates normally distribution of error and support the fact that the model fits the data adequately. These plots are very important and are required to check the normality assumption in fitted model. This will ensure that the model provides an adequate approximation to the optimization process. It is clear that there is no obvious pattern followed in the residual versus predicted response (Fig. 4b).

Fig. 5a–c shows the most relevant fitted response surfaces for the design and depicts the response surface plots of ER% versus significant variables. The curvatures of these plots indicate the interaction between the variables. The surface plots show that at low adsorbent (NiZnS-AC) and low vortex and ultrasonic time, the ER% is low. This may be attributed to the facts that when the low amount of adsorbent was used, the effective surface areas for adsorbent process of bendiocarb and promecarb, due to the decrease of the dispersion phenomena, are decreased. Also, in low value of vortex and ultrasonic

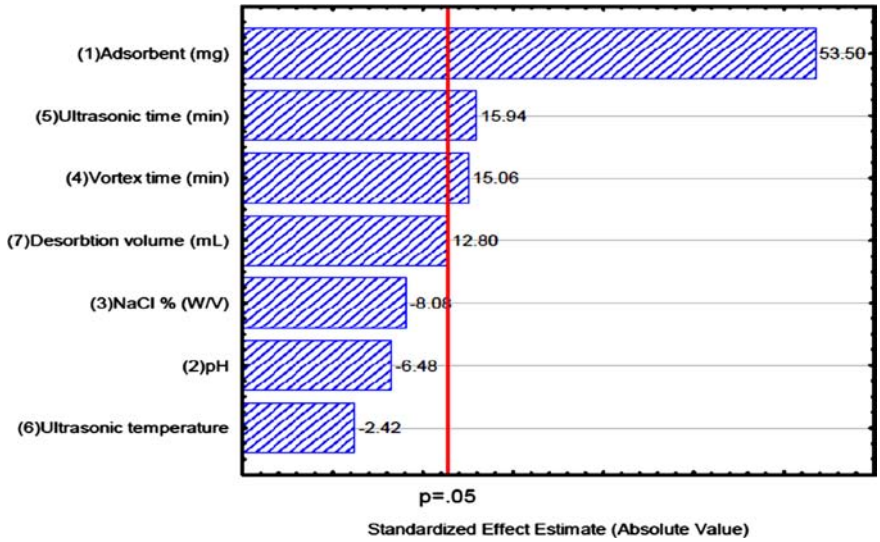


Fig. 3. Standardized main effect Pareto chart for the Plackett–Burman design of screening experiment. Vertical line in the chart defines 95% confidence level.

Table 4
Analysis of variance (ANOVA) for central composite design.

Source of variation	Sum of square	*Df*[a]	Mean square	*F*-value[b]	*P*-value
X_1	1267.276	1	1267.276	1984.926	0.014
X_2	211.889	1	211.889	331.880	0.034
X_3	244.742	1	244.742	383.338	0.032
X_1^2	209.776	1	209.776	328.570	0.035
X_2^2	158.771	1	158.771	248.681	0.040
X_3^2	44.780	1	44.780	70.139	0.076
X_1X_2	1.454	1	1.454	2.277	0.373
X_1X_3	201.503	1	201.503	315.613	0.036
X_2X_3	1.611	1	1.611	2.523	0.358
Lack of Fit	50.710	5	10.142	15.885	0.188
Pure Error	0.638	1	0.638		
Total SS	2243.409	15			

[a] Df: Degrees of freedom.
[b] Test for comparing model variance with residual (error) variance.

Table 5
Results of regression analysis for ER% of bendiocarb and promecarb.

Term	Coefficient	Standard error	*t*	*P*-value
Mean	−55.681	4.494	−12.390	0.051
X_1	9.226	0.325	28.404	0.022
X_2	13.388	0.826	16.214	0.039
X_3	14.194	0.826	17.192	0.037
X_1^2	−0.191	0.011	−18.126	0.035
X_2^2	−1.035	0.066	−15.770	0.040
X_3^2	−0.549	0.066	−8.375	0.076
X_1X_2	−0.043	0.028	−1.509	0.372
X_1X_3	−0.502	0.028	−17.765	0.036
X_2X_3	−0.112	0.071	−1.588	0.358

time there are not enough time to complete dispersion of the nanomaterial in aqueous media and subsequent mass transfer of analyte from liquid phase to solid phase (NiZnS-AC). As can be seen from Fig. 5a–c, in the middle of each variable, with respect to the opposite axial, the ER% slightly increases reaching a plateau. In general, with a glance at the results, one can conclude that the efficiency of the extraction was increased in the regions where the values of adsorbent, vortex and ultrasonic time were set at 12.0–18.0 mg, 5–7 and 5–7, respectively.

3.5. Optimization of CCD by DF

The profile for predicted values and desirability option in the STATISTICA 7.0 software is used for the optimization process. Profiling the desirability of responses involves specifying the DF for each dependent variable by assigning the predicted values to the scale with the range of 0 (undesirable) to 1 (very desirable). The CCD design matrix results (Table 2) represent the maximum (95.45%) and minimum (56.87%) average extraction recovery of the bendiocarb and promecarb. According to these values, desirability function settings for each dependent variable on ER% are depicted at the right hand side of Fig. 6. The desirability of 1.0 was assigned for maximum ER% (95.45%), 0.0 for minimum (56.87%), and 0.5 for middle (76.16%).

On the left hand side of Fig. 6 (bottom), the individual desirability scores are illustrated in such a way that for the ER%; while the desirability of 1.0 was selected as the target value, the overall response (ER%) of these plots with the observed level of each factor in the model are depicted at the top (left) of Fig. 6. These figures allow to search for evaluating the changes in the level of each variable that simultaneously affects the response (ER%) and the overall desirability of the responses.

On the basis of these calculations and the desirability score of 1, the summation ER of both bendiocarb and promecarb were optimized at 95.48% with the optimum values of the variable that was set on 15.5 mg for adsorbent (NiZnS-AC), 5.5 min for vortex, and 5.5 min for ultrasonic time. It was found that the combination of CCD and DF improved the extraction recovery of the bendiocarb and promecarb. Finally, for validation, duplicate assenting experiments were conducted using the optimized variables.

3.6. Analytical performance of the DNSUAME–HPLC–UV

A series of working solutions containing bendiocarb and promecarb at six concentration levels were prepared for the establishment of the calibration curve. For each concentration, under the optimized conditions, three replicated extractions were performed and the analytical performance of the data is listed in Table 6. At optimum conditions, DNSUAME method has linear response over 0.0033–10 $\mu g\ mL^{-1}$ with detection limit between 0.001 and 0.0015 $\mu g\ mL^{-1}$

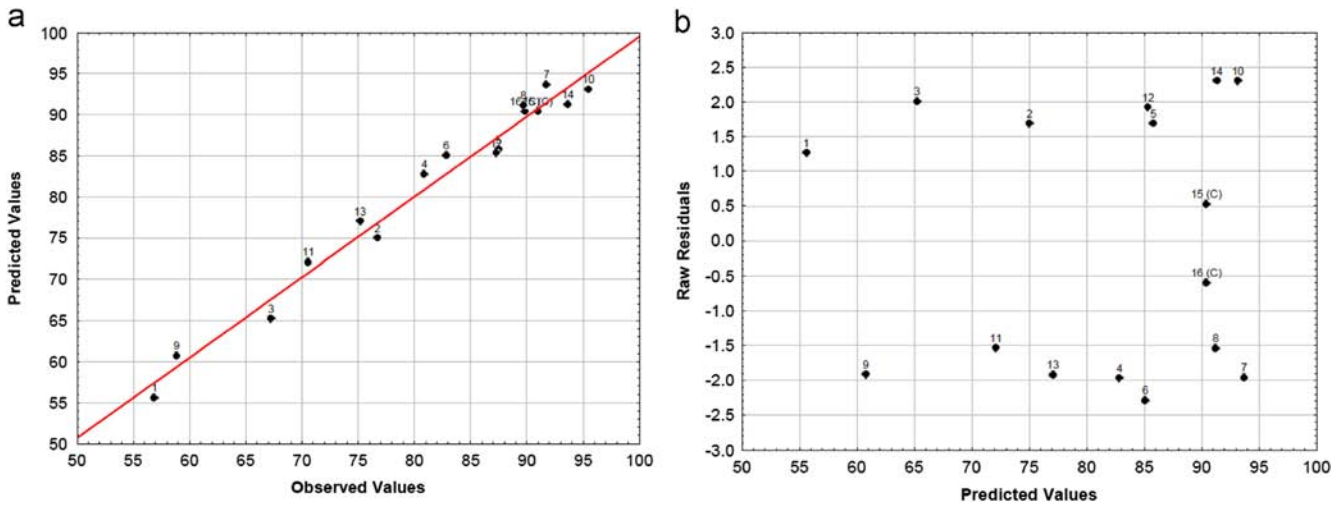


Fig. 4. (a) Plot of predicted value vs. observed value for extraction recovery of bendiocarb and promecarb. (b) Plot of residuals versus predicted response for extraction recovery of bendiocarb and promecarb.

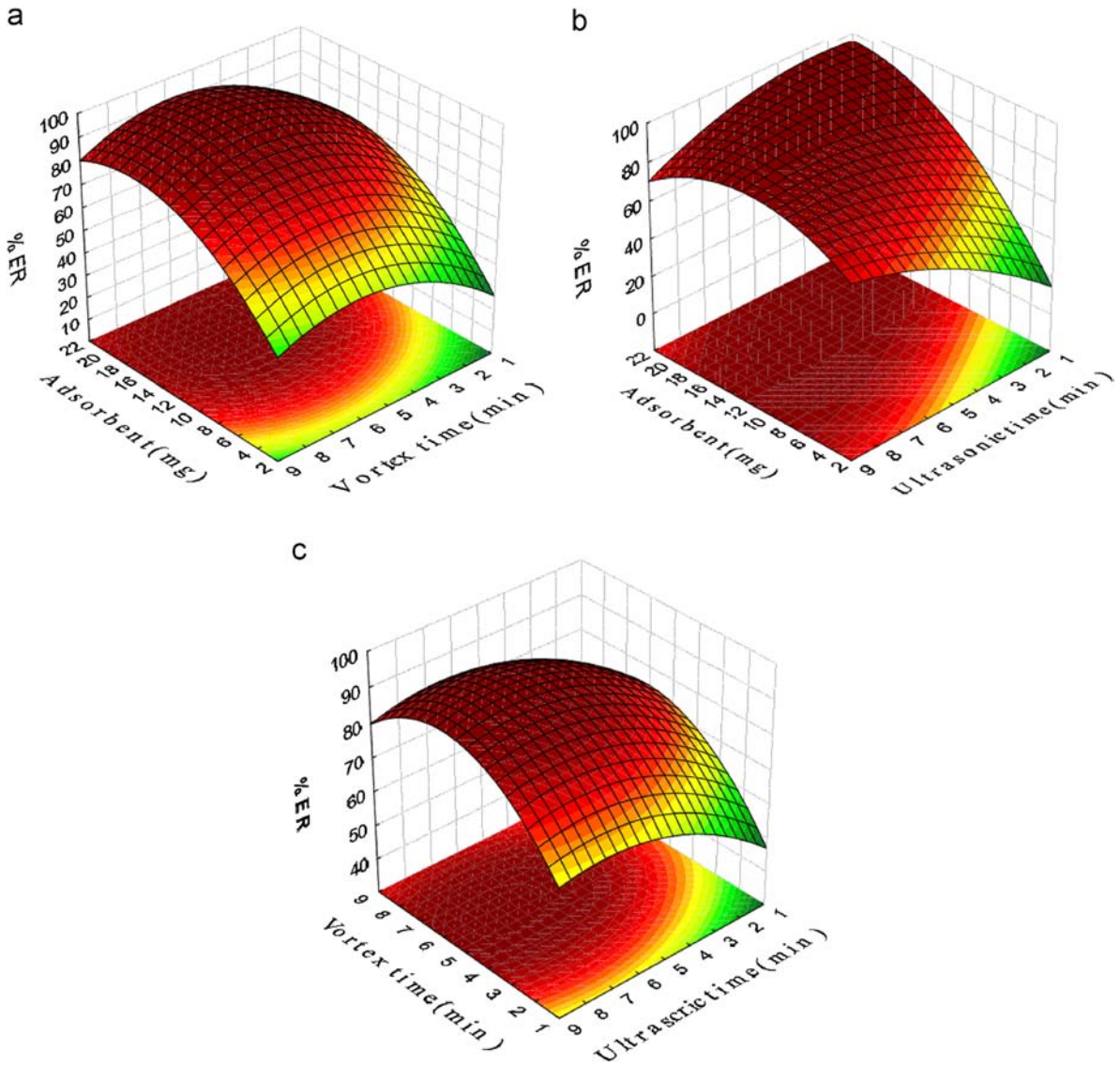


Fig. 5. Response surfaces for the 2^3 central composite designs: (a) vortex time (min)—amount of adsorbent (NiZnS-AC; mg), (b) ultrasonic time (min)—amount of adsorbent (NiZnS-AC; mg); (c) ultrasonic time (min)—vortex time (min).

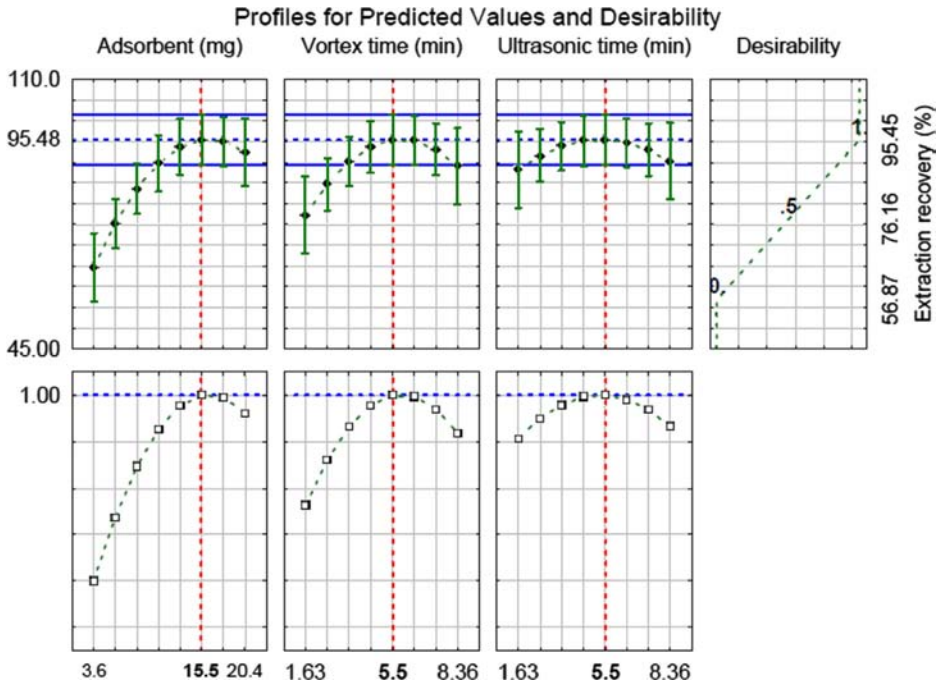


Fig. 6. Profiles for predicated values and desirability function for extraction recovery of bendiocarb and promecarb. Dashed line indicated current values after optimization.

Table 6
Analytical performance of carbamate pesticides in water samples by the DNSUAME–HPLC–UV method.

Analyte	r^2	LOD[a] ($\mu g mL^{-1}$)	LR[b] ($\mu g mL^{-1}$)	RSD[c] ($n=3$)
Bendiocarb	0.998	0.0015	0.0050–10	4.6
Promecarb	0.996	0.0010	0.0033–10	5.2

[a] Limit of detection (LOD).
[b] Linear range (LR).
[c] Relative standard deviation (RSD).

Table 7
Extraction recoveries (ER%) and relative standard deviations (RSD) in different water samples at spiked level by the DNSUAME-HPLC method.

Analyte	Spiked ($\mu g mL^{-1}$)	**Tap water**			**River water**			**Mineral water**		
		Found ($\mu g mL^{-1}$)	ER%	RSD%	Found ($\mu g mL^{-1}$)	ER%	RSD%	Found ($\mu g mL^{-1}$)	ER%	RSD%
Bendiocarb	0	–			–			–		
	0.001	0.009	91.42	5.2	0.009	89.22	4.8	0.009	93.46	4.7
	0.01	0.095	95.54	4.3	0.097	97.41	4.6	0.098	98.75	4.4
Promecarb	0	–			–			–		
	0.001	0.009	93.15	5	0.009	94.35	5.2	0.009	94.28	4.6
	0.01	0.097	97.47	4.8	0.096	96.51	4.9	0.096	96.25	3.7

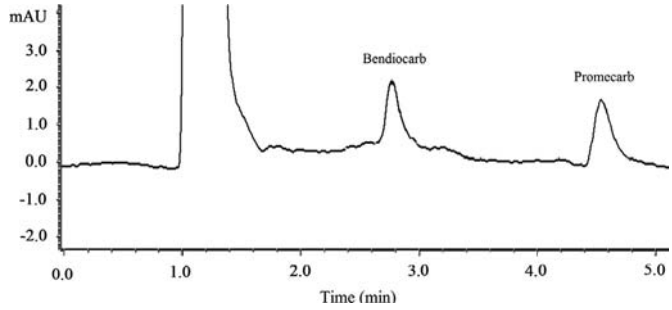


Fig. 7. Chromatograms of bendiocarb and promecarb extracted from spiked ($0.005\ \mu g\ mL^{-1}$) Beshar river water by HPLC at optimum extraction condition. Mobile phase: acetonitrile:water: (60:40, v/v); Flow rate: $1.0\ mL\ min^{-1}$; Column: C18 ($150 \times 4.6\ mm^2$, $5\ \mu m$); Room temperature; $\lambda = 220$ nm.

in water samples with the correlation determinations (r^2) ranged from 0.996 to 0.998. The repeatable study was carried out by performing three parallel replicated extractions and analyzed the concentration of $0.01\ \mu g\ mL^{-1}$ for each of the compounds under the optimal conditions. The resultant repeatability expressed as the relative standard deviations (RSDs, $n=3$) were 3.7 and 5.2% for bendiocarb and promecarb respectively. These results (Table 6) show that the proposed method has a high sensitivity and repeatability.

In order to investigate the reusability of the NiZnS-AC adsorbent, after desorption of the analytes from the adsorbent, the results showed that it was reused for the DNSUAME of the bendiocarb and promecarb. The findings showed that the NiZnS-AC adsorbent can be reused at least 8 times without a significant loss of the sorption capacity.

Table 8
Comparison of DNSUAME–HPLC–UV with other extraction methods for determination of bendiocarb and promecarb in water samples.

Method	LOD ($\mu g\ mL^{-1}$)	Linear range ($\mu g\ mL^{-1}$)	RSD (%)	Extraction time (min)	Reference
SPME–HPLC–UV	0.001	0.005–10	1.7–5.3	25	[49]
DLLME–HPLC–UV	0.0005	0.005–10	2–5	1	[50]
LPME–HPLC–UV	0.01	0.1–10	4.7–7.7	20	[51]
DLLME–LC–ESI–MS/MS	0.00002	0.001–1	1.9–9.1	1	[52]
DNSUAME–HPLC–UV	0.0005	0.0016–1	3.8–5.2	11	Present work

3.7. Analysis of water samples

In order to validate the suitability of DNSUAME method, it was revealed that the method was applied to analyze the analytes in tap, river, and mineral water samples. Among the water samples, no carbamates detected these water samples. The recoveries of the bendiocarb and promecarb were studied by spiking the carbamates standard solution into water samples at two concentrations (0.001 and 0.010 $\mu g\ mL^{-1}$). The recoveries for the bendiocarb and promecarb in tab, river, and mineral water samples were within the range of 89.22–98.75% (Table 7). Fig. 7 shows the typical chromatograms of the extracted carbamates from river water sample after being spiked at 0.005 $\mu g\ mL^{-1}$ each of the two carbamates.

In order to further demonstrate the superiority of our proposed method, a comparison of the important features of the proposed method with those reported in the literature [49–52] are given in Table 8. These results indicate that the proposed DNSUAME–HPLC–UV is a sensitive, fast, reproducible, and simple technique that can successfully be used for the preconcentration and determination of bendiocarb and promecarb in water sample.

4. Conclusion

In this research we synthesized novel nanomaterial which characterized with various methods including BET, TEM, and FT-IR. This novel adsorbent was applied for new extraction method based on DNSUAME, for the first time, as an effective method for preconcentration of bendiocarb and promecarb pesticides in environmental water samples prior to HPLC–UV. This novel nanomaterial showed great adsorptive ability towards these analytes. In this work chemometric procedure used first as a Plackett–Burman (P–B) screening design (to study the main variables that affect the DNSUAME process) and second the CCD in order to optimize the previous selected variables. DF was used to identify optimum ER% by calculating specific variables optimization simultaneously. The optimized DNSUAME combined with HPLC–UV allowed quantification of trace levels of carbamates compounds in the water samples. The advantages of the proposed method include rather easy use, fast, inexpensive, rapid and convenient extraction operation, feasibility for large-volume samples, high sensitivity, and precision and accuracy in preconcentration and determination of environmental pollutants such as carbamates.

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