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A novel dispersive micro solid phase extraction using zein nanoparticles as the sorbent combined with headspace solid phase micro-extraction to determine chlorophenols in water and honey samples by GC–ECD

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ABSTRACT

This study presents a new technique, dispersive micro solid phase extraction (DMSPE) combined with headspace solid phase micro-extraction (HS-SPME) for extraction and determination of chlorophenols (CPs) in water and honey samples using a Gas Chromatography–Electron Capture Detector (GC–ECD). Zein nanoparticles were made by liquid–liquid dispersion and applied for the first time as the sorbent phase in DMSPE. In the proposed DMSPE–HS-SPME method, 1% w/v of ethanolic zein solution was added to an aqueous sample and then a dose of the in-situ generated zein nanoparticles was applied to a pre-concentration of target analytes. Thermal desorption of analytes was performed after the isolating sorbent phase, and then HS-SPME was applied for enrichment prior to introducing to gas chromatography. All the important parameters influencing efficiency of the extraction process such effects of salt, pH, sorbent concentration, temperature, sorbent solution volume in DMSPE procedure, extraction temperature, extraction time, desorption temperature and time in the HS-SPME procedure were investigated and optimized. Results showed that under optimum extraction conditions, detection limits (signal to noise ratio=3) were in the range of 0.08–0.6 ng mL^{-1} and evaluations for relative standard deviations (RSDs %) were between 6.62% and 8.36%.

1. Introduction

Chlorophenols (CPs) are organic environmental pollutants generated from degradation of industrial, biogeochemical and pesticide products. CPs are included in lists of major pollutants by the U.S. Environmental Protection Agency (EPA) and the European Union. In recent years, several clean-up methods have been tested to remove pre-concentrations of CPs from water samples such as solid phase extraction (SPE) [1–5], solid phase micro-extraction (SPME) [6–13], liquid phase micro-extraction (LPME) [14–21], dispersive liquid–liquid micro-extraction (DLLME) [22,23], SPE-DLLME [24] and stir-bar sorptive extraction (SBSE) [25–30]. Dispersive solid-phase extraction (DSPE), is a relatively new technique for clean-up operations; the pre-concentration method is based on solid phase extraction methodology that was introduced by Anastassiades et al. [31] in 2003, it is a very efficient procedure used to increase selectivity in analytical processes. More recently, dispersive solid-phase micro-extraction has been reported as a miniaturization model of DSPE based on use of micro amounts at the sorbent phase [32,33]. In both of these techniques, the solid sorbent is added directly to an extract without processes of sample manipulation such as conditioning, so the clean-up procedure relies only on shaking and centrifugation. C18 and carbon nanotubes (CNTs) are commonly used materials for application in the sorbent phase of such processes.

In this study, zein is introduced as the active material in the sorbent phase for pre-concentration and determination of CPs. Zein is considered as a natural, inexpensive and environmental compatible protein, it is the predominant protein in corn and

Abbreviations: DMSPE, dispersive micro solid phase extraction; HS-SPME, headspace solid phase microextration; CPs, chlorophenols; DSPE, dispersive solid-phase extraction; MWCNTs, multi-walled carbon nanotubes; PVC, poly vinyl chloride

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contains many non-polar hydrophobic amino acid residues including many sulfur-containing amino acids. Zein proteins are hydrophobic and insoluble in water. Conventionally, aqueous ethanol (60–70%) is used to dissolve zein [34–36]. During the past few decades, studies on this biopolymer and its applications have received considerable attention in several scientific fields and various industries because of naturally occurring properties if zein such as high aliphatic indexes and surface hydrophobicity. Zein also has many potential applications in food and pharmaceutical industries including tablet coating and free-standing packaging materials [37], drug encapsulants [38], emulsifiers [39] and antioxidants [40].

This study presents a novel application of zein nanoparticles as a sorbent phase in dispersive micro solid phase extraction (DMSPE). Also tested was application of the process to matrix removal, preconcentration of chlorophenols from water and food samples. Conventional dispersive solid phase micro-extraction procedures use a solid sorbent to extract analytes from samples but this proposed method used an ethanolic solution of zein for dispersion in aqueous samples. The first stage of the process was to generate nano particles; zein particles were solidified in aqueous solution in nano scale by dispersing the polymer solution in an aqueous sample. The next stage was to separate the generated nanoparticles from the aqueous solution by applying a centrifugal force. Then the process was followed by HS-SPME using laboratory-made PVC/MWCNT nanocomposite SPME fiber. Finally, CPs were enriched by exposing the SPME fiber to the headspace of the precipitated solid zein nanoparticles. To the best of our knowledge, there are no other reports to date on application of zein in the analytical field and particularly, in sample preparations. To our knowledge this paper is the first to introduce application of zein nanoparticles for extraction of CPs (model compounds) as a sorbent in DMSPE and its combination with HS-SPME.

2. Experimental

2.1. Chemicals and reagents

Zein biopolymer powder was purchased from Sigma. Analytical-grade methanol, ethanol, tetrahydrofuran (THF), sodium chloride, hydrochloric acid and sodium hydroxide were obtained from E. Merck (Darmstadt, Germany). Chlorophenols (2,3-dichlorophenol, 2,4-dichlorophenol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, 2,3,6-trichlorophenol and pentachlorophenol) and high-molecular-weight poly vinyl chloride (PVC) were purchased from Fluka. MWCNTs used in the present study were kindly gifted from the University of Mazandaran (Babolsar, Iran). Nitrogen and hydrogen, (99.999% purity) were from Sabalan Oxygen Co., (Tehran, Iran). Stainless steel wire was purchased from Azar electrode Co., (Urmia, Iran).

2.2. Apparatus

Gas chromatographic analyses were performed on an Agilent gas chromatograph system model 6890N (Agilent Technologies, Wilmington, DE, USA) equipped with an electron capture detector (ECD) and a split/splitless injector system. Chromatographic separation was done on an Agilent tapered liner (4 mm i.d.) with a SPB-50 (cross bond 50% – phenyl polysiloxane) capillary column (30 m × 0.5 mm i.d., film thickness 0.5 μm) (Supelco, USA).

The temperature program applied to separate analytes was as follows: temperature of the primary column was maintained at 80 °C for 1 min, and then raised from 15 °C min^{-1} to 200 °C and maintained for 1.5 min and then raised again to reach 280 °C at the rate of 30 °C min^{-1} and then maintained at that temperature for 4.5 min. Nitrogen (99.999%,) was used as a carrier and make-up gas with flow rates of 3–45 mL min^{-1}. Injector and detector temperatures were set between 215 and 250 °C. The sample injection was made using splitless mode. ChemStation software was used for data acquisition and processing. A Labinco BV model L-81 hot plate-stirrer (Labinco, Breda, Netherlands) was used to control temperature and for sample agitation. A Metrohm 744 pH meter (Metrohm, Herisau, Switzerland) was used to adjust pH level. A laboratory-made SPME device was used in all experiments. The Hettich centrifuge (D-78532, Germany) was utilized for acceleration of phase separation. Transmission electron micrograph (TEM) was recorded for characterization and morphology measurements of the zein nanoparticles using a Philips CM 100 Biotwin Electron Microscope (the Netherlands) operated at 75 kV.

2.3. Preparation of a PVC/MWCNTs nanocomposite SPME fiber

Preparation of the SPME fiber used in this study was described in a previous study [41]. Briefly, 50 mg of MWCNTs was poured into a solution of 10 mg PVC powder in 5 mL THF and mixed well (83:17 w/w %). After a few minutes, THF was evaporated as long as a viscose suspension of PVC/MWCNTs nano-composite was formed. One centimeter of steel wire (total length 2 cm) was mounted on a laboratory-made SPME device and introduced several times into the suspension of PVC/MWCNTs. After evaporation of THF at room temperature, a highly porous and robust coating (3.1 μm thickness) of PVC/MWCNTs nano-composite formed on the wire. The proposed SPME fiber was then conditioned at 200 °C for 20 min to remove any fiber contamination.

2.4. Dispersive micro solid phase extraction and solid phase micro-extraction procedure

Zein solution (10% W/V) was prepared in 85% – ethanol. 5 mL aqueous solution (pH 1.5) containing proper chlorophenols (50 ng mL^{-1}) was transferred into a 15 mL glass tube with PTFE septum. After addition of appropriate amount of sodium chloride, 1 mL of the as prepared zein solution was injected into the solution by syringe and the cloudy solution was gained as a result of formation and dispersion of zein nanoparticles in the solution. Later, this cloudy solution was centrifuged at 3000 rpm for 10 min to separate the zein nanoparticles from the liquid phase. Subsequently, liquid phase was removed and septum was inserted into the glass tube and SPME fiber was exposed to the head space of precipitated zein nanoparticles in a sealed glass at 60 °C. After 15 min, fiber was drawn back into the needle immediately and then transferred into the injection port of the GC with no delay (in less than 5 s) and then desorption of analytes was performed at 215 °C for 4 min. A schematic diagram of the DMSPE–SPME process is presented in Fig. 1.

3. Result and discussion

3.1. Preparation of zein nanoparticles

Recently reported is preparation of zein nanoparticles based on the liquid–liquid dispersion process by Zhong and coworker [42]. The reported preparation process is based on an addition of zein solution (ethanol/water) to water and emulsifying the zein solution into smaller droplets. A decrease in ethanol concentration caused the zein to be insoluble and to change its formation to nano-scaled particle. Generation of dispersed zein nanoparticles was confirmed by transmission electron-microscopy (TEM) (Fig. 2). Due to presence of various functional groups in the structure of zein biopolymer, nanoparticle showed great potential for

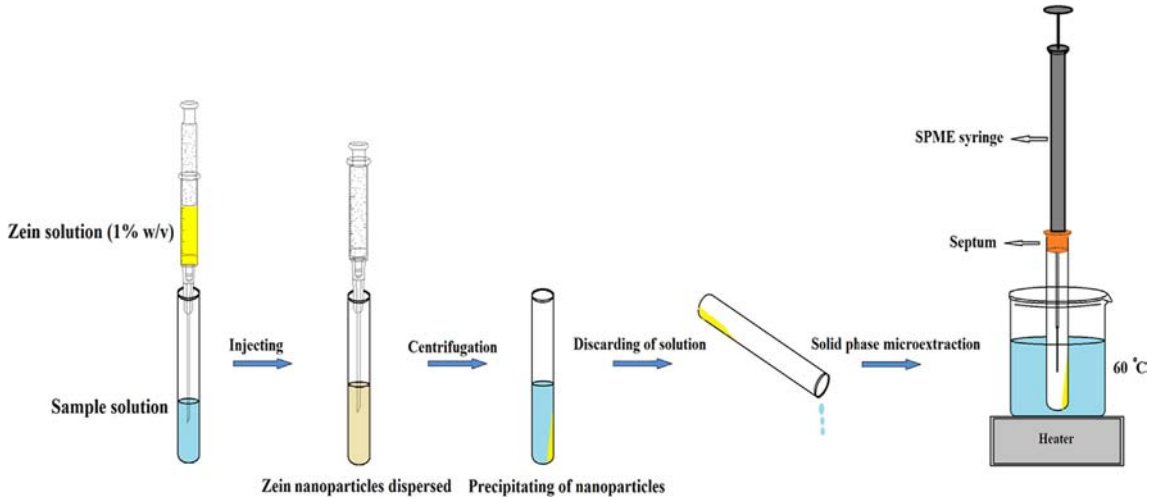

Fig. 1. Schematic diagram of DMSPE–SPME procedure.

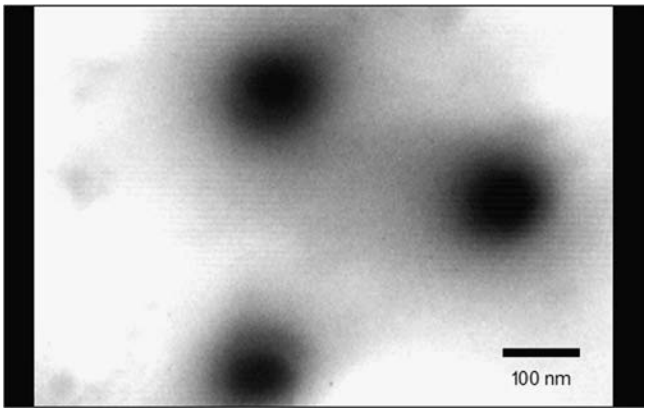

Fig. 2. TEM image of zein nanoparticles prepared in DMSPE step (solution pH 1.5, NaCl 5 mol L^{-1}).

extraction of analytes from water samples. Accordingly, this work introduces a novel application of zein nanoparticles in preconcentration of chlorophenols in aqueous solutions as a model analytes and a new sample preparation method, DMSPE for the first time.

3.2. Optimization of DMSPE procedure

3.2.1. Effect of salt addition

The effect of salt addition on extraction efficiency of chlorophenols was investigated by testing additions of sodium chloride to the aqueous solution in the range of 0.5–5 mol L^{-1}. The addition of salt plays an important role in formation and aggregation of dispersed zein nanoparticles by facilitating precipitation of sorbent nanoparticles and improving separation from the liquid phase under centrifugal force. Moreover, it is well known that addition of salt is sufficient to enhance activity of the coefficient of components in aqueous solutions and increases the tendency of solutes to migrate during the aqueous phase. Fig. 3 displays the effect of salt addition on extraction efficiency of chlorophenols and demonstrates that the maximum extraction efficiency was obtained at 5 mol L^{-1} sodium chloride. Hence, that concentration was selected for further experiments.

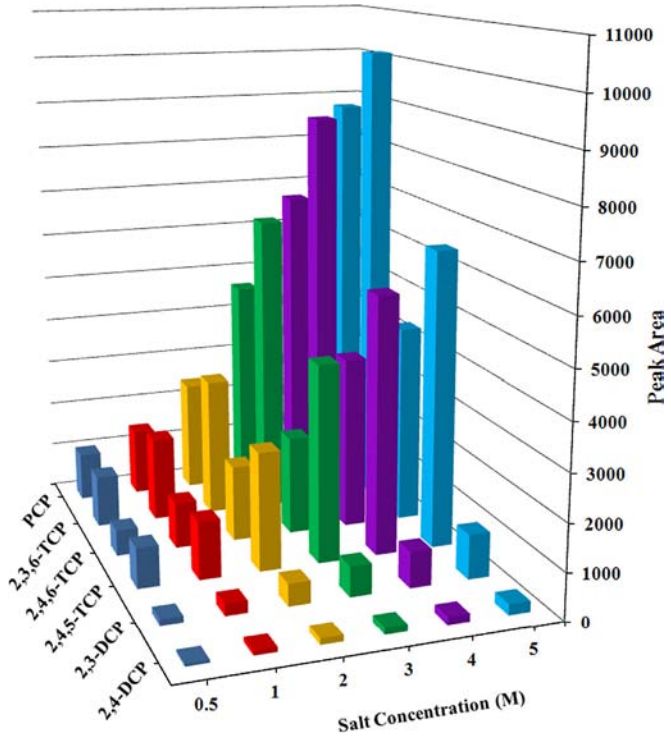

Fig. 3. Effect of salt addition on the extraction efficiency of chlorophenols: extraction conditions: 5 mL sample; pH 1.5.

3.2.2. Effect of solution pH

The pH level of a solution is one of the most important parameters for extraction of acidic or basic components. Generally, pH values affect extraction efficiency by changing the charge of analytes. Typically, higher extraction efficiency can be obtained in an aqueous sample when analytes are in neutral molecular form. CP(s) are weak acids with lower pH values than those that exist in neutral form and higher pH values in an anionic structure. Thus, extraction efficiency of CPs could be reduced at a basic pH value. The effect of solution pH was tested in the range of 1.5–9 (Fig. 4). As seen, the extraction efficiency of all CPs increased as the pH value decreased. In order to obtain high level extraction efficiency and low detection limit values, pH 1.5 was chosen for subsequent experiments. It should be noted that, due to the poor solubility of

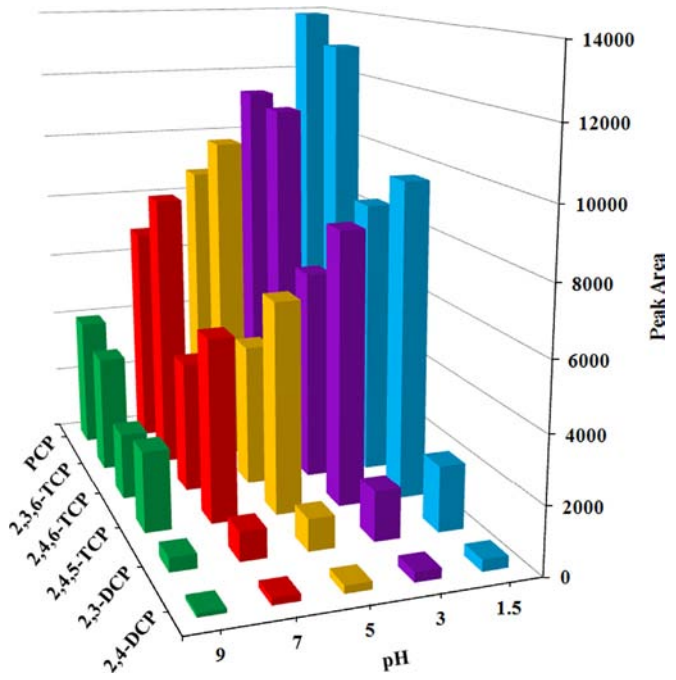

Fig. 4. Effect of pH value on the extraction efficiency of chlorophenols: extraction conditions: 5 mL sample; salt concentration, NaCl 5 mol L^{-1}.

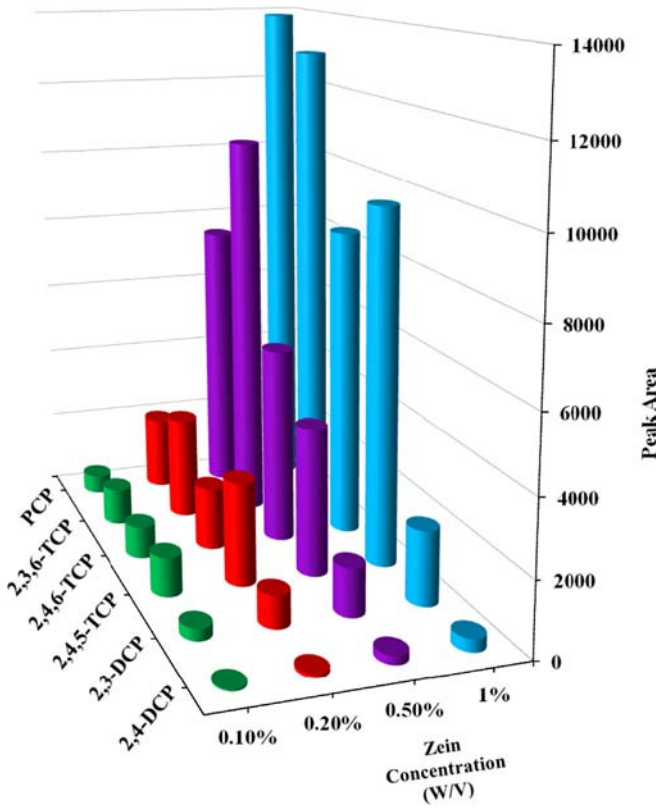

Fig. 5. Effect of zein concentration on the extraction efficiency of chlorophenols: extraction conditions: 5 mL sample; salt concentration, NaCl 5 mol L^{-1}; 1 mL zein solution with different concentrations; pH 1.5.

zein in an acidic medium, the dispersed zein nanoparticles were easily precipitated, results also showed fast separation from the liquid phase at the chosen pH level.

3.2.3. *Effect of the amount of zein nano-sorbent*

The influence of zein quantity on recovery was also investigated. Therefore, different amounts of sorbent (dissolved in 1 mL 85% ethanol solution) were added in the range of 0.1–1% w/v to 5 mL of sample solutions. The results obtained are shown in Fig. 5. According to expectations, recovery values increased with increasing amounts of zein. Based on the results obtained in these tests, 1% w/v of zein solution was chosen as the optimum concentration for the sorbent. As zein solutions were cloudy at concentration levels higher than 1% w/v, effects at higher concentrations than that were not tested.

3.2.4. *Effect of zein solution volume*

To examine the effect of nano-sorbent solution volume on extraction efficiency, various volumes of 85% ethanolic solution containing 1% w/v of zein (0.5–2 mL) were added to 5 mL sample solutions. As shown in Fig. 6, extraction efficiency values increased according to increased volume of alcoholic zein solution up to 1 mL and then diminished at higher volumes, this result was probably due to a higher rate dissolution of zein in the liquid phase by increasing the amount of ethanol in the mixture. As a result, 1 mL of 1% w/v zein solution was selected as the optimum volume for further experiments.

3.2.5. *Effect of solution temperature on extraction efficiency*

Temperature is an effective parameter on extraction equilibrium in the proposed dispersive micro solid phase extraction method and it can change the distribution constant of the analytes between a liquid sample solution and the solid zein nanoparticles. Moreover, solubility of zein in the liquid phase is temperature-dependent. Thus, the effect of temperature on extraction of the studied analytes was tested at various solution temperatures in

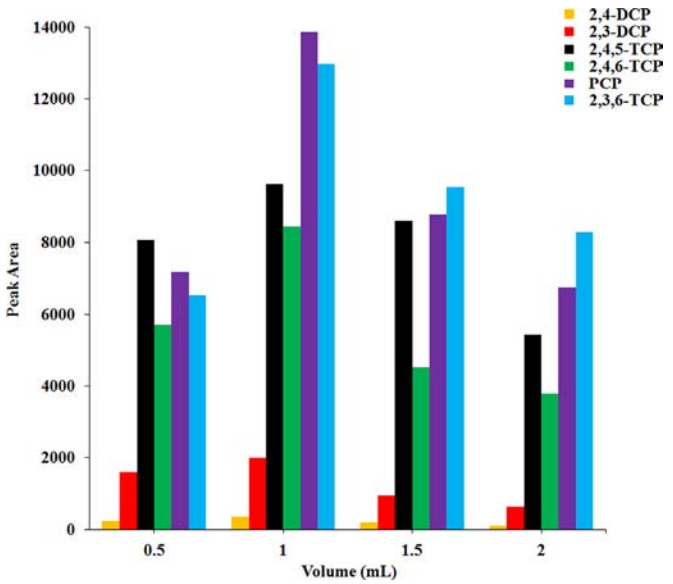

Fig. 6. Effect of zein solution volume on the extraction efficiency of chlorophenols: extraction conditions: 5 mL sample; salt concentration, NaCl 5 mol L^{-1}; pH, 1.5; zein concentration, 1% w/v.

the range of 10–50 °C. According to these results (Supplementary data 1), it can be inferred that lower and higher temperatures had an unfavorable effect on amount of extracted analytes in comparison with processes done at conventional room temperature. Therefore, room temperature was selected for the subsequent experiments.

3.3. Optimization of SPME procedure

3.3.1. Effect of temperature and time

Temperature has a more important effect on the proposed micro extraction method because thermal desorption of analytes from the precipitated nanoparticles and their sorption by SPME fiber are dependent on temperature. It is obvious that complete desorption of all compounds can occur at much higher temperatures. However, selection of an optimal value for this parameter has a major impact on extraction yield due to the dual effect of temperature on the SPME procedure and a decrease in extraction efficiency at higher values. Therefore, several different temperatures were tested ranging from 20 °C to 70 °C. Fig. 7 depicts the effect of SPME temperature on extraction efficiency of chlorophenols. A review of the resulting peak areas in relation to temperature confirmed that most of the components had been extracted at 60 °C. The effect of exposure time on extraction efficiency was also studied in the range of 2 –20 min (Supplementary Data 2). Referring to the obtained results, equilibrium was reached in 15 min. Accordingly, the fiber was exposed to head space of the separated zein nanoparticles for 15 min in subsequent extractions.

3.3.2. Effect of desorption temperature and time on extraction

In order to quantitatively transfer analytes to GC through SPME, both desorption temperature and time must be optimized. For this purpose, injections were performed at high temperature ranging from 150 to 215 °C. Also, several periods of time were tested (0.5, 1, 2, 3, 4 and 5 min) in order to optimize desorption time. The obtained results revealed that the temperature program (215 °C within 4 min) was the optimal desorption condition that provided the highest values for peak areas.

3.4. Analytical performances

Repeatability of the newly developed method was examined by five replicated analyses of chlorophenolic compounds at 50 ng mL^{-1} level using a single fiber. Results revealed that RSD% of the method was less than 8.36% for all model analytes. This result confirmed repeatability of the proposed method. Quantitative characteristics of the proposed method such as linear dynamic ranges (LDR), correlation coefficient of calibration graphs, and detection limits of target compounds are listed in Table 1. The obtained calibration graph for 2,4-DCP was linear and in the concentration range of 2–100 ng mL^{-1}. This method showed a wider dynamic linear range from 1 to 100 ng mL^{-1} for quantitative detection of other studied CPs. The correlation coefficients of all calibration graphs were satisfactory ($R^2 > 0.9950$). Evaluations for limit of detections (LODs) (S/N ratio of 3:1) were between 0.08 and 0.6 ng mL^{-1}. Evaluations for analytical performance characteristics of the proposed method are summarized in Table 2 and compared with some other reported micro extraction methods in related literature. Results demonstrated that the proposed DMSPE–HS-SPME method for determination of CPs in the present work showed a low or similar LOD and RSD% in most cases, or even superior in some cases in comparison with results from previously reported methods.

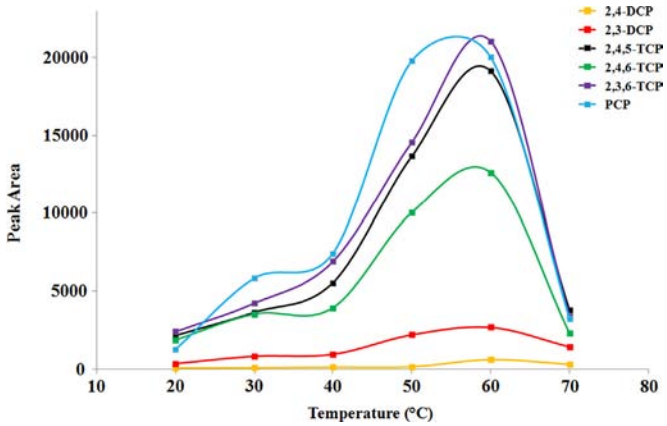

Fig. 7. Effect of SPME temperature on the extraction efficiency of chlorophenols: extraction conditions: 5 mL sample; salt concentration, NaCl 5 mol L^{-1}; pH, 1.5; zein concentration, 1% w/v; extraction solution temperature, 25 °C (DMSPE conditions).

Table 1
Analytical performance data of the proposed method.

Compound	(ng mL^{-1})		R^2	Repeatability (RSD[c] %, $n=5$)
	LOD[a]	LDR[b]		
2,4-DCP	0.6	2–100	0.9996	7.24
2,3-DCP	0.3	1–100	0.9987	8.05
2,4,5-TCP	0.08	1–100	0.9982	7.53
2,4,6-TCP	0.1	1–100	0.9989	8.29
2,3,6-TCP	0.08	1–100	0.9995	6.62
PCP	0.08	1–100	0.9959	8.36

[a] Limit of detection ($S/N=3$).
[b] Linear dynamic range.
[c] Relative standard deviation.

3.5. Analysis of real samples

In order to evaluate feasibility of the presented method for extraction and determination of chlorophenols, some water samples (waste water and river water samples) and honey samples were analyzed. The river water samples were taken from the "Aras river" (Iran) and wastewater samples were collected from a local food factory. The DMSPE step was performed on a 5 mL of sample waters (pH 1.5, NaCl 5 mol L^{-1}). For honey, 0.25 g of sample was dissolved in 5 mL of NaCl solution (5 mol L^{-1}, pH=1.5) and the following steps were taken. The obtained quantitative results and spiked recovery values are presented in Table 3. Recovery data shown in Table 3 demonstrates that the proposed method had no significant matrix effect on determination of CPs in real samples. Typical chromatograms regarding water, wastewater, honey and CPs standard mixture samples are shown in Fig. 8. Chlorophenolic compounds were detected in all samples; however, some concentration levels were under the LOQs of this proposed method.

4. Conclusion

In this research, a novel application of zein nanoparticles (produced by in-situ liquid–liquid dispersion procedure) was introduced as a sorbent phase in dispersive micro solid phase extraction. The proposed micro extraction procedure was combined with headspace solid phase micro extraction in order to increase sensitivity of the method. Combination of DMSPE procedure based on zein nanoparticles and SPME procedure, as a well-known sample preparation method, offers some important advantages such as properties that are more environmentally-friendly and the method is fast and inexpensive. Finally, the proposed method was successfully utilized to determine CPs in water and food samples after optimizing all the effective parameters.

Table 2
Comparison of DMSPE–HS-SPME–GC–ECD with other microextraction methods for determination of chlorophenols.

Method	LOD[a] (ng mL^{-1})	Extraction time (min)	Sample volume (mL)	RSD[b] %	Derivatization	References
SPE–GC–ECD	0.003–0.110	17	100	< 10	Yes	[12]
SDME–GC–MS	0.20–0.28	25	5	2.4–6.3	Yes	[26]
SBSE–GC–MS	0.1–0.4	45	10	6–27	Yes	[32]
SPME–GC–MS	0.02–0.05	30	7	6.8–10	Yes	[20]
DLLME–GC–ECD	0.01–2	A few seconds	5	0.6–4.7	Yes	[29]
SPE-DLLME–GC–ECD	0.0005–0.1	< 10	100	1.1–6.4	Yes	[31]
DMSPE–HS-SPME–GC–ECD	0.08–0.6	Less than 5 s	5	6.62–8.36	No	Proposed method

[a] LOD: limit of detection.
[b] RSD: relative standard deviation.

Table 3
Result of real samples analysis.

Compound	Waste water sample				River sample				Honey sample			
	$C_{initial}$	C_{added}	($C_{found} \pm SD$)[a]	Recovery %	$C_{initial}$	C_{added}	($C_{found} \pm SD$)[a]	Recovery %	$C_{initial}$	C_{added}	($C_{found} \pm SD$)[b]	Recovery %
2,4-DCP	55.79	10	64.90 ± 4.67	91	37.44	10	47.01 ± 3.76	96	50.41	10	61.30 ± 3.01	109
2,3-DCP	46.73	10	57.50 ± 3.96	107	10.45	10	21.05 ± 0.89	106	ND[c]	10	9.20 ± 0.51	92
2,4,5-TCP	20.11	10	30.86 ± 2.35	107	3.29	10	13.90 ± 0.68	106	ND	10	9.43 ± 0.80	94
2,4,6-TCP	20.95	10	30.36 ± 2.54	94	3.71	10	14.05 ± 0.76	103	ND	10	10.68 ± 0.61	107
2,3,6-TCP	24.14	10	33.74 ± 1.44	96	4.35	10	14.09 ± 0.77	97	ND	10	9.54 ± 0.76	95
PCP	32.05	10	41.75 ± 3.45	97	11.58	10	20.97 ± 0.89	94	ND	10	9.47 ± 0.81	95

[a] $C \pm SD$ (ng mL^{-1}, $n=3$).
[b] $C \pm SD$ (ng g^{-1}, $n=3$).
[c] ND = not detected.

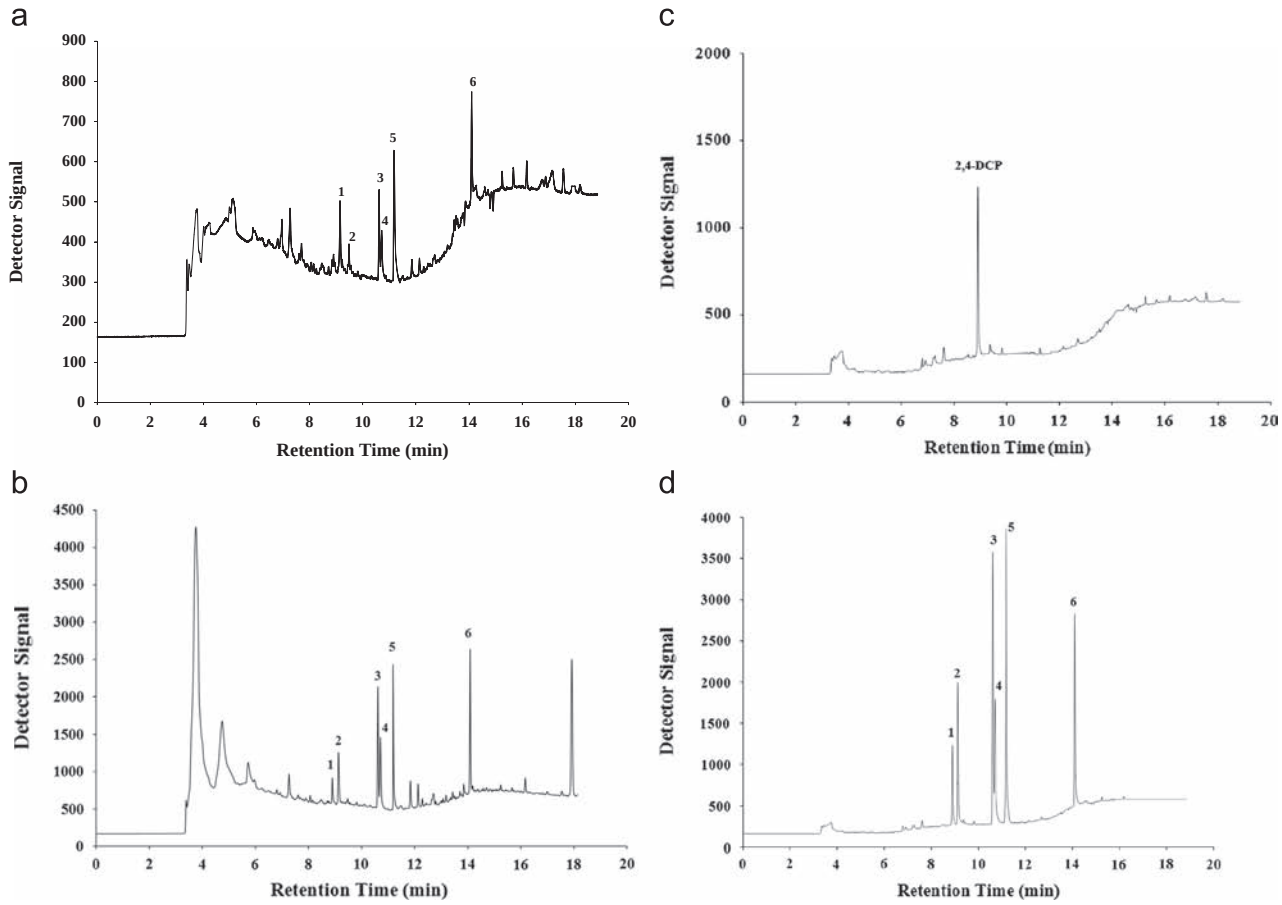

Fig. 8. Typical chromatograms of (a) river water sample (b) wastewater sample (c) honey sample and (d) standard mixture of the chlorophenols at concentration levels of 2,4-DCP and 2,3-DCP, 100 ng mL^{-1}; 2,4,5-TCP, 2,4,6-TCP, 2,3,6-TCP and PCP, 25 ng mL^{-1}. Peak numbers correspond to (1) 2,4-DCP, (2) 2,3-DCP, (3) 2,4,5-TCP, (4) 2,4,6-TCP, (5) 2,3,6-TCP, and (6) PCP.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2014.06.002.

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