http://dx.doi.org/10.5935/0103-5053.20150185

J. Braz. Chem. Soc., Vol. 26, No. 10, 2046-2053, 2015.
Printed in Brazil - ©2015 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Dispersive Liquid-Liquid Microextraction Based on Solidification of Floating Organic Drop with Central Composite Design for the Determination of Nitrophenols Using High-Performance Liquid Chromatography

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A simple and practical pre-concentration method, dispersive liquid-liquid microextraction based on solidification of a floating organic drop (DLLME-SFO) technique, was proposed for the determination of 4-nitrophenol and 2-nitrophenol in water samples. The effective experimental parameters on the extraction efficiency such as extraction solvent volume, dispersive solvent volume, and pH were studied using the response surface methodology. Under the optimum experimental conditions, the pre-concentration factors of 116 and 100 for 2-nitrophenol and 4-nitrophenol were obtained, respectively. The calibration curves were linear in the range of 5-150 μg L^{-1} with the detection limit of 1.70 μg L^{-1}. The proposed method was successfully applied to the determination of nitrophenols in water samples.

Keywords: central composite design, dispersive liquid-liquid microextraction, nitrophenols, solidification of organic drop

Introduction

Nitrophenolic compounds are some of the most common pollutants in aquatic environments. These compounds are typically toxic and degrade extremely slowly. They mainly originate from chemical, agricultural, medical, and other industries.[1] These compounds have received considerable attention in waste water and environmental analysis programs due to the hazards they pose to human health, even at micrograms *per* liter levels,[2] so that their determination at trace level is of great importance.[3-5] The European community (EC) specifies a legal tolerance level of 0.1 μg L^{-1} for each phenolic compound and 0.5 μg L^{-1} for the sum of all phenolic compounds in water intended for human consumption.[6] Therefore, developing a simple and rapid method for determination of these compounds in the environment is crucial.

A number of methods are available for the analysis of nitrophenols in water, most of which couple a pre-concentration technique with gas chromatography (GC)[7,8] and/or high performance liquid chromatography (HPLC).[9,10] In many analytical methods, sample preparation is usually necessary to determine trace analytes in samples. Recently, various pretreatment techniques have been reported for extraction of phenolic compounds from aqueous samples, such as solid phase extraction (SPE),[11] solid phase microextraction (SPME),[12-14] single drop microextraction (SDME)[15] and hollow fiber liquid phase microextraction (HF-LPME).[16]

However, regular SPE requires large volumes of toxic solvent, column conditioning and a process that is complicated and time-consuming.[17] Meanwhile, although SPME is solvent free, simple and fast, it is more expensive and its fibers are fragile. Further, it has a limited life time, and also sample carry-over in this method can be a problem.[18,19] The main drawbacks of SDME include instability and volatility of the extraction solvent.[20] Although HF-LPME is simple and consumes a small amount of organic solvent, the extraction time needed in this technique is usually long.[21] Therefore, the development of environmentally friendly pretreatment methods is necessary to overcome such disadvantages.

Dispersive liquid-liquid microextraction (DLLME) is an analytical technique recently introduced by Assadi and co-workers.[22] This technique is based on injection of extraction solvent (immiscible in water) assisted by dispersive solvent (miscible in both water and extraction solvents) within an aqueous solution which generates a

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very large surface area between the fine droplets of the extraction solvent and the aqueous sample. The main advantages of this technique are simplicity, rapidity of operation, high enrichment factor, and low consumption of extraction solvent. A novel DLLME based on the solidification of floating organic drop (DLLME-SFO) was introduced by Leong *et al.*[23] In this method, solvents with the densities lower than water are used and the floated extractant is solidified and easily collected for analysis. Since its introduction, DLLME has been successfully used for the extraction and determination of different phenolic compounds because of its rapidity, simplicity and high extraction efficiency.[24-27]

The central composite design (response surface) is used for efficient optimization of the main experimental variables in the extraction procedure. This method is a multivariate optimization technique that produces a detailed quantitative model for the response(s). The model can predict how a response relates to the values of various factors and usually requires fewer experiments compared to a one-at-a-time procedure.[28]

In this study, DLLME-SFO followed by HPLC was applied for determination of nitrophenols in water samples. The effect of main experimental variables on the extraction procedure was investigated and optimized by the experimental design method.

Experimental

Reagents

4-Nitrophenol (99.5%), 2-nitrophenol (99.5%), HPLC grade solvents acetonitrile, acetone, methanol, 1-undecanol and 1-decanol were obtained from Merck (Darmstadt, Germany). The ultra-pure water (six times distillated) used was purchased from Shahid Ghazi Pharmaceutical Co. (Tabriz, Iran). Stock solutions of nitrophenols (1000 μg mL^{-1}) were prepared in methanol and stored in a freezer at −10 °C. The working standards were prepared by subsequent dilutions of stocks.

Instrumentation

Chromatographic analysis was carried out by Knauer HPLC with Chromgate software version 3.1 having binary pumps Smartline 1000-1 and Smart line 1000-2, and Smartline UV 2500 variable wavelength programmable detector (Berlin, Germany), online solvent vacuum degasser and manual sample injection with a 20 μL injection loop (model 7725i, Rheodyne, Cotati, CA, USA). Separations were carried out on an H5-ODS C18 column (15 cm × 4.6 mm, with 5 μm particle size) from Anachem (Luton, UK). A mixture of water/methanol (40:60 v/v) at a flow rate of 1.0 mL min^{-1} was used as a mobile phase in isocratic elution mode, and the detection was performed at the wavelength of 280 nm. A centrifuge (Hettich, EBA 20, Tuttlingen, Germany) was used for centrifuging.

Sample preparation

Well water samples were collected from Kermanshah (Iran) in glass bottles and stored in the dark at 4 °C. Waste water samples were collected from Kermanshah petrochemical company (Iran). The samples were filtered through a filter paper, stored at 4 °C and analyzed within 2 days after collection.

DLLME-SFO procedure

For the DLLME-SFO, an aliquot of 5.0 mL of aqueous solution (KCl 1% m/v) containing 50 μg L^{-1} of each nitrophenol was placed in a 10 mL screw cap glass tube with conic bottom. Then, a mixture of 500 μL methanol (dispersive solvent) containing 40 μL 1-undecanol (extraction solvent) was injected rapidly into the sample solution by a gastight 2.50 mL syringe (Hamilton, Nevada, USA). A cloudy solution, resulting from the dispersion of the fine 1-undecanol droplets in the aqueous solution, was formed in the test tube. After centrifugation for 5 min at 4800 rpm, the fine 1-undecanol droplets floated at the top of the test tube. Then, the glass tube was transferred into the ice bath, and the solidified organic solvent was transferred into the conical vial where it melted quickly at room temperature and was injected into the HPLC system for analysis.

Results and Discussion

In this work, DLLME-SFO combined with HPLC was used for simultaneous extraction and pre-concentration of two nitrophenols in water samples. In order to obtain high extraction efficiency, the procedure conditions such as type of the extraction and dispersive solvents as well as their volumes, sample pH and salt concentration were optimized. The enrichment factor (EF) was defined as the ratio of the analyte concentration in the collected phase to the analyte concentration in the aqueous sample, where the analyte concentration in the collected phase was calculated from the direct calibration graph (0.1-5.0 mg L^{-1}) of nitrophenols in methanol. An experimental central composite design was used for the optimization of the main variables affecting the extraction efficiency.

One factor at a time optimization

Selection of extraction solvent

Selecting a suitable extraction solvent is of great importance in DLLME technique to obtain efficient recovery. This solvent must possess some properties such as lower density than water, low solubility in water, extraction capability of compounds of interest, good chromatographic behavior and a melting point near room temperature (in the range of 10-30 °C). In this work, 1-undecanol (d = 0.83 g mL^{-1}, mp = 19 °C) and 1-decanol (d = 0.83 g mL^{-1}, mp = 6.4 °C) were examined as extraction solvents. The results revealed that 1-undecanol has better extraction efficiency than 1-decanol (Figure 1). Therefore, 1-undecanol was selected as the extraction solvent because of its suitable melting point and good chromatographic behavior. Moreover, after the centrifugation step, 1-undecanol can be collected better than 1-decanol.

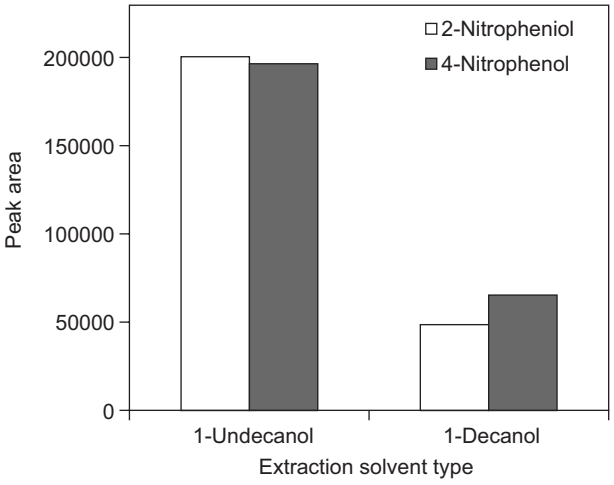

Figure 1. Effect of type of extraction solvent on the extraction efficiency of nitrophenols. Extraction conditions: extraction solvent volume, 40 µL; dispersive solvent, 0.5 mL methanol; sample volume, 5.0 mL; pH, 4.9; salt concentration, 1% (m/v); concentration of both analytes, 50 µg L^{-1}.

Selection of dispersive solvent

Miscibility of dispersive solvent in the extraction solvent and aqueous phase is the most important factor for selecting the dispersive solvent.[29] Several dispersive solvents including methanol, acetonitrile, acetone, and ethanol were tested for this purpose. The chromatographic signal of acetone was so high that it interfered with the analysis of target analytes, while the solubility of 1-undecanol in acetonitrile was not adequate. In addition, the extraction efficiency of nitrophenols with ethanol as a dispersive solvent was lower than that in methanol. In comparison with other dispersive solvents, the use of methanol resulted in higher peak area in the case of both analyets (Figure 2). Therefore, methanol was chosen as the dispersive solvent in the following studies.

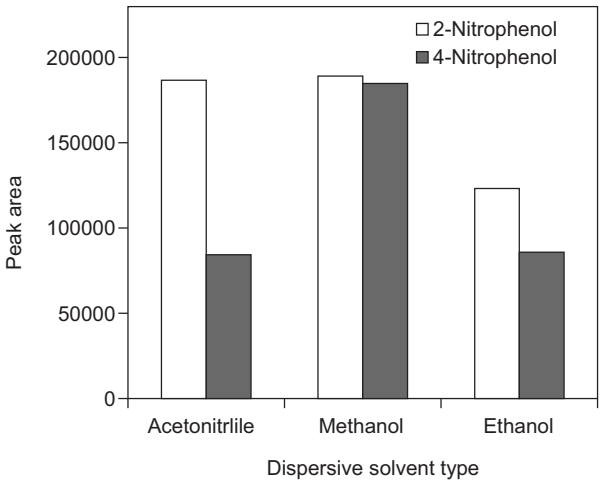

Figure 2. Effect of type of dispersive solvent on the extraction efficiency of nitrophenols. Extraction conditions: extraction solvent, 40 µL 1-undecanol; dispersive solvent, 0.5 mL; sample volume, 5.0 mL; pH, 4.9; salt concentration, 1% (m/v); concentration of both analytes, 50 µg L^{-1}.

Effect of salt addition

Generally, the increase of the ionic strength can cause a decrease in the solubility of the analytes in the aqueous phase and, consequently, enhance extraction efficiency. Therefore, the effect of salt concentration on the nitrophenols extraction efficiency was studied by adding different amounts of KCl (0-5% m/v). It was found that the salt addition up to 1% (m/v) caused an improvement in the formation of floating drops, resulted in increased extraction efficiency of the nitrophenols, and leveled off at higher salt concentrations (Figure 3). Therefore, 1% (m/v) salt was chosen as the optimum concentration for subsequent experiments.

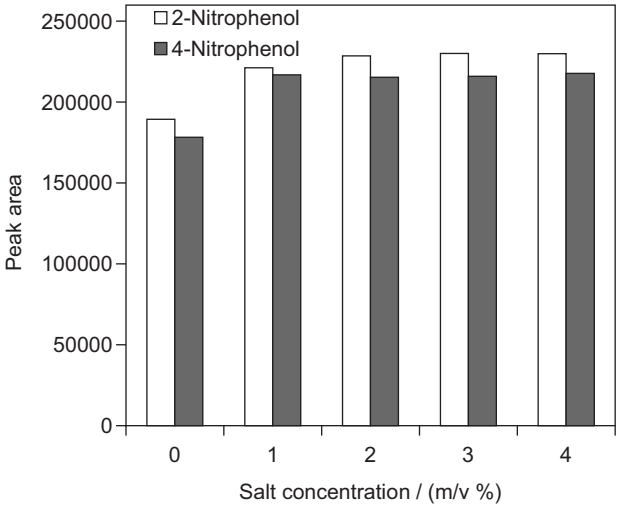

Figure 3. Effect of amount of KCl on the extraction efficiency of nitrophenols. Extraction conditions: extraction solvent, 40 µL 1-undecanol; dispersive solvent, 0.5 mL methanol; sample volume, 5.0 mL; pH, 4.9; concentration of both analytes, 50 µg L^{-1}.

Experimental design

In order to perform systematic investigation of the effect of the most effective independent variables and their possible interactions on the responses (peak areas), the response surface methodology was carried out. Three variables including, extraction solvent volume (X_1), dispersive solvent volume (X_2), and pH (X_3), were considered to build the regression models between the variables and chromatogram peak area of 2-nitrophenol and 4-nitrophenol.

A face-centered central composite design (CCD) was selected to design the experiments. For three variables (n = 3), the central composite design can be represented by points on a cube, including 2^n cubic points, 2n axial or star points and a few replicates of the center point in order to estimate the experimental error. The cubic points implicate a full two level factorial design with coded values of −1 and +1 (−1 and +1 indicate lower and upper levels of each variable, respectively). The axial points define the points at which two variables are in their central level (coded as 0) and other variables situated at a distance from the center of the design ($-\alpha$ and $+\alpha$). For a face-centered central composite design, $|\alpha|$ is equal to 1 and therefore each variable is studied at three different levels.[30] Preliminary experiments were carried out and, subsequently, lower and upper levels for extraction solvent (30 and 50 µL), dispersive solvent (0.5 and 1.5 mL) and pH (4 and 7) were selected. The actual and coded values of variables for 18 designed experimental sets along with the observed values of related peak area of nitrophenols are summarized in Table 1.

The Design-Expert software (Trial Version 8.0.0, Stat-Ease Inc., Minneapolis, MN, USA) was used to compare the analysis of variance (ANOVA) results of various regression models including linear, quadratic and cubic models. Among the evaluated models, the reduced cubic models resulted in appropriate equations for the responses of both nitrophenols. The coefficients of regression equations are listed in Table 2. The significance of each regression term was determined by *p*-value. With the confidence level of 95%, if the absolute probability of regression term *p*-value is lower than 0.05, the corresponding term will have a significant effect on the response.

Table 1. Design matrix for three variables (actual and coded levels) with the observed response

Run	X1 Extraction solvent / µL	X2 Dispersive solvent / mL	X3 pH	Observed peak area of 4-NP	Observed peak area of 2-NP
1	30 (−1)	0.5 (−1)	4 (−1)	140	103
2	50 (+1)	0.5 (−1)	4 (−1)	71	55
3	30 (−1)	1.5 (+1)	4 (−1)	113	138
4	50 (+1)	1.5 (+1)	4 (−1)	95	131
5	30 (−1)	0.5 (−1)	7 (+1)	50	102
6	50 (+1)	0.5 (−1)	7 (+1)	48	44
7	30 (−1)	1.5 (+1)	7 (+1)	62	73
8	50 (+1)	1.5 (+1)	7 (+1)	30	48
9	30 (−1)	1 (0)	5.5 (0)	122	111
10	50 (+1)	1 (0)	5.5 (0)	88	67
11	40 (0)	0.5 (−1)	5.5 (0)	180	189
12	40 (0)	1.5 (+1)	5.5 (0)	123	98
13	40 (0)	1 (0)	4 (−1)	136	157
14	40 (0)	1 (0)	7 (+1)	49	105
15	40 (0)	1 (0)	5.5 (0)	141	150
16	40 (0)	1 (0)	5.5 (0)	154	157
17	40 (0)	1 (0)	5.5 (0)	141	145
18	40 (0)	1 (0)	5.5 (0)	145	162

NP: nitrophenol.

Table 2. The least-squares fit and parameter estimates (significance of regression terms)

Term	4-NP			2-NP		
	Term estimate	MS	*p*-value	Term estimate	MS	*p*-value
Intercept	141.9	–	–	147.3	–	–
X_1	−15.5	2402.5	0.0026[a]	−18.2	3312.4	0.0020[a]
X_2	−28.5	1624.5	0.0066[a]	−45.5	4140.5	0.0011[a]
X_3	−31.6	9985.6	< 0.0001[a]	−21.7	4708.9	0.0008[a]
X_1X_2	2.6	55.1	0.4826	9.25	684.5	0.0553
X_1X_3	6.6	351.1	0.1079	−3.5	98.0	0.4038
X_2X_3	−0.4	1.1	0.9184	−17	2312.0	0.0048[a]
X_1^2	−33.5	3047.4	0.0014[a]	−52.0	7333.7	0.0002[a]
X_2^2	13.0	455.4	0.0750	2.5	16.6	0.7243
X_3^2	−46.0	5742.6	0.0003[a]	−12.5	425.0	0.1107
$X_1^2X_2$	−10.1	820.1	0.0278[a]	−1	8.0	0.8061
$X_1X_2X_3$	27.4	1199.0	0.0130[a]	56.2	5062.5	0.0007[a]

[a]Significant at 95% confidence limit; NP: nitrophenol; MS: mean squares.

It can be seen from Table 2 that linear terms of variables and quadratic term of the extraction solvent are highly significant for both 4-nitrophenol and 2-nitrophenol extraction. No binary interactions between the variables were observed for 4-nitrophenol, while in the case of 2-nitrophenol, only X_2X_3 interaction was significant at 95% confidence limit. Considering confidence limits for selection of regression terms, the mathematical equation describing the relationship between coded values of the variables and responses could be reduced to the following equations:

$$R\ (4\text{-Nitrophenol}) = 144.0 - 15.5X_1 - 28.5X_2 - 31.6X_3 - 28.9X_1^2 - 41.4X_3^2 - 10.1X_1X_2X_3 + 27.4X_1^2X_2$$

$$R\ (2\text{-Nitrophenol}) = 144.8 - 18.2X_1 - 45.5X_2 - 21.7X_3 - 17.0X_2X_3 - 57.6X_1^2 + 56.2X_1^2X_2$$

Statistics ANOVA results for these models are presented in Table 3. As seen, the F-value of lack of fit (LOF) of 5.1 and 4.0 for 4-nitrophenol and 2-nitrophenol, respectively, indicated that the LOFs were not significant relative to the pure errors. The R-squared of 0.9566 and 0.9389 showed a good fitness of observed data to the obtained models. Additionally, the prediction R-squared of 0.8270 and 0.8194 for 4-nitrophenol and 2-nitrophenol, respectively, were in acceptable agreement with the R-squared and showed a high predictive power of both models.

Table 3. ANOVA results for the reduced cubic model of 4-nitrophenol and 2-nitrophenol

Source	SS	df	MS	F-value	*p*-value
4-Nitrophenol					
Model	32056.2	7	4579.5	31.5	< 0.0001
Residual	1453.5	10	145.4	–	–
Lack of fit	1340.8	7	191.5	5.1	0.1043
Pure error	112.8	3	37.6	–	–
R^2: 0.9566, adjusted R^2: 0.9262, predicted R^2: 0.8270					
2-Nitrophenol					
Model	30118.31	6	5019.7	28.2	< 0.0001
Residual	1956.8	11	177.9	–	–
Lack of fit	1787.8	8	223.5	4.0	0.1422
Pure error	169	3	56.3	–	–
R^2: 0.9389, adjusted R^2: 0.9057, predicted R^2: 0.8194					

SS: sum of squares; df: degree of freedom; MS: mean squares.

The obtained models can be simply plotted as three-dimensional surfaces representing the peak area of each nitrophenol as a function of two independent variables (see Figure 4). In fact, presentation of the three-dimensional response surfaces indicates the entire main effects and the interaction between the variables. According to the results, the effect of variables and optimum conditions for both nitrophenols are similar. The plots of the predicted responses *versus* observed values for the peak area of nitrophenols are shown in Figure 5. As can be seen, the observed values could best be predicted by applying the regression equations.

In order to simultaneously optimize the experimental variables to have maximum possible responses for both nitrophenols, desirability function with equal weights for the responses was considered. Finally, the value of 40 μL for extraction solvent volume, 0.5 mL for dispersive solvent volume and 4.9 for pH were introduced as optimum values and the subsequent experiments were performed at these conditions.

Analytical performance

The analytical characteristic data for the proposed method are summarized in Table 4. As is obvious, the calibration graphs for both analytes were linear over the concentration range of 5-150 μg L^{-1}. Under the optimum experimental conditions, limit of detection (S/N = 3) was 1.7 μg L^{-1}. Moreover, the enrichment factors and the correlation coefficient (r^2) were found to be in the range of 100-116 and 0.9890-0.9950, respectively.

Analysis of real samples

The proposed method was applied for simultaneous extraction and determination of nitrophenols in water samples. Two types of water (well water and waste water) were analyzed by HPLC-UV after DLLME-SFO procedures. The samples were then spiked with analytes standard solutions at different levels to assess matrix effects and the corresponding relative recoveries, and the results are summarized in Table 5. The chromatograms of the blank and the spiked wastewater samples with the analytes under the optimum conditions are shown in Figure 6.

Comparison of the proposed DLLME-SFO method with other methods

The proposed DLLME-SFO method was compared with other published methods including, IL-DLLME,[26] USAEME-HPLC-UV[31] and DLLME-HPLC.[25] As can be seen from Table 6, the LODs of this method are about the same as those reported methods. The enrichment factor of 2-nitrophenol is higher than those previously reported methods. Also, this technique used the experimental design

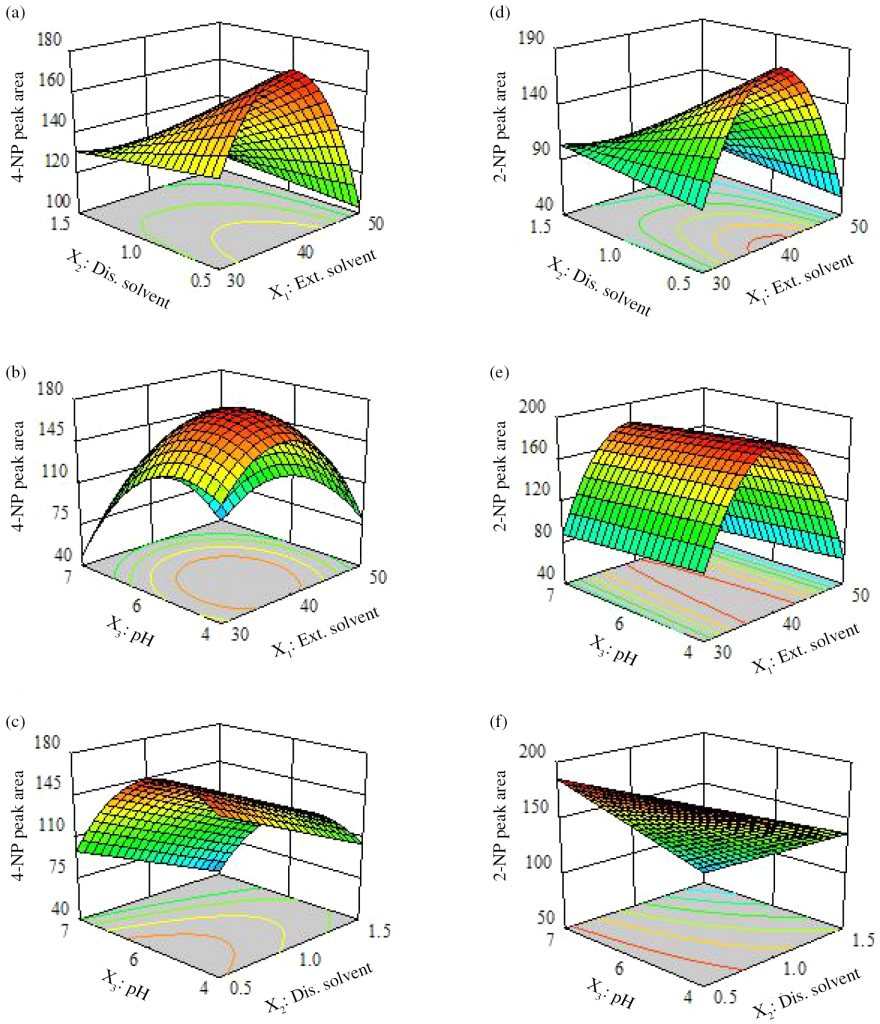

Figure 4. Three-dimensional response surfaces of chromatogram peak area of 4-nitrophenol (a, b, c) and 2-nitrophenol (d, e, f) *versus* independent variables. Each response surface is plotted at the optimum value of the remaining variable.

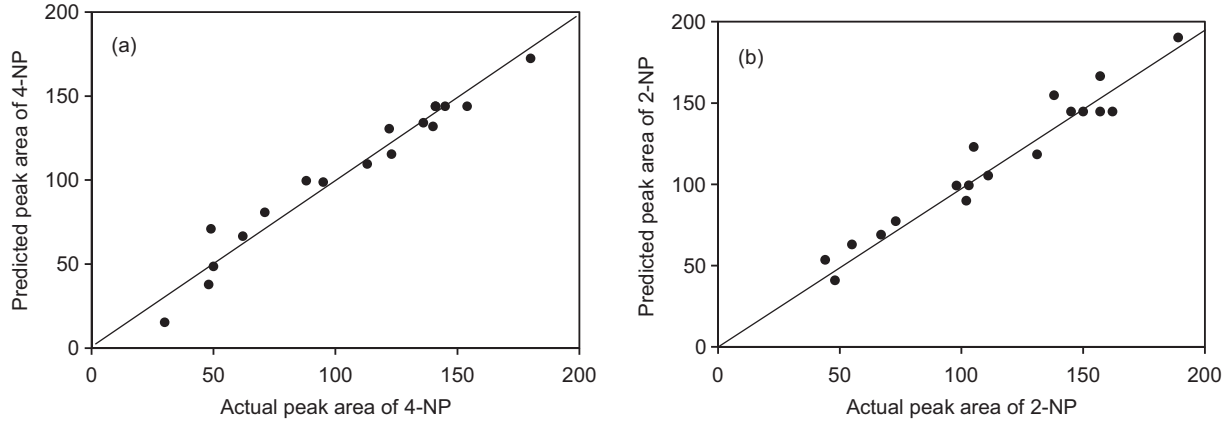

Figure 5. Plot of predicted *versus* observed values for peak area of 4-nitrophenol (a) and 2-nitrophenol (b).

method to investigate the effect of main experimental variables on the extraction procedure. All these results reveal that DLLME-SFO is a fast and simple technique that can be used for pre-concentration and determination of nitrophenols in water samples.

Conclusions

In this study, DLLME-SFO combined with HPLC-UV has been evaluated for simultaneous extraction and determination of nitrophenols in water samples. To reach

Table 4. Performance characteristics of the DLLME-SFO procedure

Analyte	LR / (μg L^{-1})	$R^{2\,a}$	LOD / (μg L^{-1})	EF
2-Nitrophenol	5.0-150	0.9890	1.7	116.0
4-Nitrophenol	5.0-150	0.9950	1.7	100.0

[a]Square of correlation coefficient; LR: linear range; LOD: limit of detection (S/N = 3); EF: enrichment factor. Extraction conditions: extraction solvent, 40 μL 1-undecanol; dispersive solvent, 0.5 mL methanol; sample volume, 5.0 mL; pH, 4.9; salt concentration, 1% (m/v) KCl.

Table 5. Determination of nitrophenols in water samples by the proposed method

Sample	Added / (μg L^{-1})		Found / (μg L^{-1})		Relative recovery / %	
	2-NP	4-NP	2-NP	4-NP	2-NP	4-NP
Well water	0	0	< LOD	< LOD	–	–
	15	25	14.17 ± 1.01[a]	24.40 ± 1.30	94.44	97.60
Waste water	0	0	< LOD	< LOD	–	–
	25	50	21.93 ± 0.67	51.03 ± 1.10	87.73	102.07

[a]Mean found amount ± standard deviation (n = 3); NP: nitrophenol; LOD: limit of detection. Extraction conditions: extraction solvent, 40 μL 1-undecanol; dispersive solvent, 0.5 mL methanol; sample volume, 5.0 mL; pH, 4.9; salt concentration, 1% (m/v) KCl.

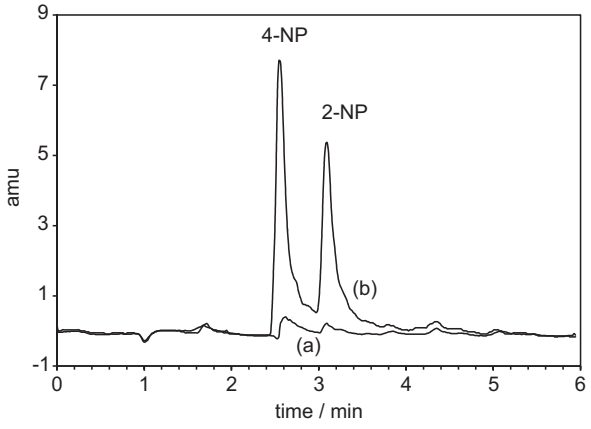

Figure 6. Chromatogram of blank sample (a) and chromatogram of spiked waste water sample (b) at concentration levels of 25 μg L^{-1} for 2-nitrophenol, 50 μg L^{-1} for 4-nitrophenol. Extraction conditions: extraction solvent, 40 μL 1-undecanol; dispersive solvent, 0.5 mL methanol; sample volume, 5.0 mL; pH, 4.9; salt concentration, 1% (m/v) KCl.

a high extraction efficiency, the procedure conditions were optimized and the effect of main variables studied by central composite design. This method is simple, rapid and provides high efficiency and low organic solvent-consumption.

Acknowledgements

The authors thank the research council of Razi University (Kermanshah, Iran) for financial support.

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Table 6. Comparison of DLLME-SFO-HPLC with other extraction methods for determination of nitrophenols

Method	Analyte	LR / (μg L^{-1})	LOD / (μg L^{-1})	EF	Reference
IL-DLLME	4-NP	20-400	1.25	–	26
USAEME-HPLC	2-NP	2-200	1	103	31
	4-NP	1-200	0.25	175	
DLLME-HPLC	2-NP	0.5-500	0.4	97	25
	4-NP	0.5-200	0.3	37	
DLLME-SFO-HPLC	2-NP	5-150	1.70	116	This work
	4-NP	5-150	1.70	100	

LR: linear range; LOD: limit of detection; EF: enrichment factor; NP: nitrophenol.

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Submitted: May 19, 2015
Published online: July 24, 2015