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ORIGINAL PAPER

Determination of 11 priority pollutant phenols in wastewater using dispersive liquid—liquid microextraction followed by high-performance liquid chromatography—diode-array detection

Mohammad Saraji · Mehdi Marzban

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Abstract Dispersive liquid—liquid microextraction coupled with high-performance liquid chromatography—diode-array detection was applied for the extraction and determination of 11 priority pollutant phenols in wastewater samples. The analytes were extracted from a 5-mL sample solution using a mixture of carbon disulfide as the extraction solvent and acetone as the dispersive solvent. After extraction, solvent exchange was carried out by evaporating the solvent and then reconstituting the residue in a mixture of methanol–water (30:70). The influences of different experimental dispersive liquid—liquid microextraction parameters such as extraction solvent type, dispersive solvent type, extraction and dispersive solvent volume, salt addition, and pH were studied. Under optimal conditions, namely pH 2, 165-μL extraction solvent volume, 2.50-mL dispersive solvent volume, and no salt addition, enrichment factors and limits of detection ranged over 30–373 and 0.01–1.3 μg/L, respectively. The relative standard deviation for spiked wastewater samples at 10 μg/L of each phenol ranged between 4.3 and 19.3% (n=5). The relative recovery for wastewater samples at a spiked level of 10 μg/L varied from 65.5 to 108.3%.

Keywords Dispersive liquid–liquid microextraction · Liquid chromatography · Wastewater analysis · Priority pollutant phenols

M. Saraji (✉) · M. Marzban
Department of Chemistry, Isfahan University of Technology, Isfahan 84156-83111, Iran
e-mail: saraji@cc.iut.ac.ir

Introduction

Phenols are present in aquatic environments because of their wide use in many industrial processes, such as production of plastics, dyes, drugs, pesticides, antioxidants, and paper, as well as petrochemical processes [1, 2]. The interest in determining phenolic compounds is due to their toxicity and persistence. For this reason, 11 common phenols are on the US Environmental Protection Agency list of priority pollutants [3, 4].

A number of methods are available for the analysis of phenols in water, most of which couple a preconcentration technique with gas chromatography (GC) [5–7] and/or high-performance liquid chromatography (HPLC) [8, 9]. Methods based on GC usually need a derivatization step before analysis [6, 7]. On the other hand, HPLC has advantages for the determination of phenolic compounds because no derivatization process is required.

Extraction is a prerequisite to isolating and preconcentrating analytes prior to chromatographic analysis. Different sample preconcentration methods have been developed over the past few decades. Since the introduction of single-drop microextraction (SDME) in 1996 [10], various solvent microextraction approaches have been developed. Two types of solvent microextraction techniques, i.e., SDME and membrane-based liquid-phase microextraction (LPME), are widely used [11], in which analytes are extracted from aqueous samples into a few microliters of a solvent. Although these methods are simple, fast, and inexpensive, yielding high enrichment factors [11–15], they have disadvantages such as instability of the solvent drop, formation of air bubbles in the hollow-fiber LPME, time-consuming extraction procedure, failure in most cases to easily attain equilibrium even after a long time, and low precision [11–16].

Rezaee et al. [17] developed a novel LPME technique named dispersive liquid–liquid microextraction (DLLME). In this method, an appropriate mixture of extraction and dispersive solvents is rapidly injected into the aqueous sample by a syringe to form a cloudy solution. The analyte in the sample is extracted into the fine droplets of the extraction solvent. After extraction, phase separation is performed by centrifugation and the enriched analyte in the sedimented phase is determined by chromatography or spectrometry methods. The advantages of this novel method include very short extraction time, ease of operation, low cost, and high enrichment factors. Since its introduction, DLLME has been successfully used for the extraction and determination of analytes of different chemical nature, such as polycyclic aromatic hydrocarbons, aromatic amines, decabrominated diphenyl ether, volatile phenols, organophosphorous pesticides, chlorobenzenes, chlorophenols, triazine herbicides, trihalomethanes, anilines, chloramphenicol, phthalate esters, fatty acids, antioxidants, and tetracyclines [17–25]. Despite the advantages of DLLME, it is not well suited to extraction from samples with complex matrices (i.e., biological and wastewater samples) [25], and most of the literature on this has focused on extraction of analytes from relatively clean samples such as river water [25].

In this study, the suitability of DLLME combined with HPLC for the determination of 11 priority pollutant phenols in wastewater samples was assessed. Parameters affecting the extraction efficiency (kind and volume of extraction and dispersive solvent and sample ionic strength) were investigated. The method was validated under the best condition using industrial wastewater samples.

Experimental

Materials

A standard mixture of 11 phenols containing phenol (Ph), 4-nitrophenol (4-NP), 2-chlorophenol (2-CP), 2,4-dinitrophenol (2,4-DNP), 2-nitrophenol (2-NP), 2,4-dimethylphenol (2,4-DMP), 4-chloro-3-methylphenol (4-C-3-MP), 2,4-dichlorophenol (2,4-DCP), 2-methyl-4,6-dinitrophenol (2-M-4,6-DNP), 2,4,6-trichlorophenol (2,4,6-TCP), and pentachlorophenol (PCP) at a concentration of 2,000 mg/L in methanol was purchased from Restek (Bellefonte, PA, USA).

A standard solution at a concentration of 20 mg/L using methanol as the solvent was prepared weekly. Diluted working solutions were prepared daily from this solution by dilution with HPLC water. Water samples were filtered through 0.45-μm nylon membranes (Millipore, Bedford, MA, USA). The stock solution of internal standard was prepared by dissolving 10.1 mg of 2-chloro-5-methylphenol in 10 mL methanol.

HPLC-grade methanol, water, acetone, and acetonitrile were purchased from Caledon Laboratories (Georgetown, ON, Canada). Extraction solvents, CS_2 (99%), CCl_4 (99%), and $C_2Cl_3F_3$ (98%), were purchased from Merck (Darmstadt, Germany). Other reagents and solvents were also obtained from Merck.

HPLC analysis

Chromatographic analysis was performed using a Hewlett-Packard 1090-II liquid chromatograph (now Agilent, Palo Alto, CA, USA) equipped with a UV–vis diode-array detector. The system was equipped with a Rheodyne 7125i injector with a 20-μL loop. A LiChrospher 100RP-18 (5-μm, 125 mm×4-mm inner diameter) column (Merck, Darmstadt, Germany) connected to a guard column (10 mm×4 mm, 5 μm) was used for separation.

The separation was performed using an acetonitrile–water gradient. The mobile phase consisted of acetonitrile (solvent A) and water (solvent B) adjusted to pH 2.8 with sulfuric acid. The gradient program was as follows: 0–3 min, 20% solvent A; 15 min, 55% solvent A; 19 min, 80% solvent A; and 21 min, 90% solvent A. A washing period of 6 min with 90% solvent A and a re-equilibration period of 10 min with 20% solvent A were used between individual runs. The mobile phases were constantly degassed using helium sparging and used at a flow rate of 1.0 mL/min. The detections were performed at 200 nm for Ph, 2-CP, 2,4-DMP, and 4-C-3-MP; at 285 nm for 2-NP and 2,4-DNP; at 230 nm for 2,4-DCP and 2,4,6-TCP; at 270 nm for 2-M-4,6-DNP and internal standard; at 210 nm for PCP; and at 302 nm for 4-NP.

Extraction procedure

A 5.00-mL water sample (acidified with sulfuric acid at pH 2) spiked with an appropriate amount of the compounds studied was placed in a 10-mL screw-cap glass test tube with a conical bottom. Acetone (as the dispersive solvent; 2.50 mL) containing 165 μL CS_2 (as the extraction solvent) was injected rapidly into the sample solution by a 5.00-mL gastight syringe (Hamilton, Bonaduz, Switzerland). The sample was then gently shaken for 5 s until a cloudy solution formed in the test tube. After centrifugation of the mixture at 3,500 rpm for 4 min, the extraction phase settled at the bottom of the conical test tube. The sedimented phase (144 μL) was transferred into another test tube with a conical bottom using a 250-μL HPLC syringe. Then, 5 μL of triethylamine (TEA) and 10 μL of internal standard solution (10 mg/L) were added to the test tube. The organic phase was evaporated to dryness with a gentle stream of nitrogen gas. The residue was dissolved in 25 μL of water–methanol mixture (3:7) and a 20-μL aliquot was injected into the HPLC system for analysis.

Wastewater samples

The wastewater samples were collected from four different wastewater treatment plants of Isfahan Mobarakeh Steel Company. Samples 1, 2, and 3 were collected from local primary treatment plants of the manufacturing units. The influent compositions of these wastewater treatment plants are a mixture of the usual chemical compounds used in the steel making industry, such as different kinds of surfactants and cleaning agents. Sample 4, which was collected from the final effluent of the wastewater treatment plant of Isfahan Mobarakeh Steel Company, was a mixture of industrial and domestic wastewater. The chemical oxygen demands of all the samples were between 20 and 60 mg/L. All the samples were filtered through 0.45-μm membrane filters (nylon membrane filter, Millipore, Bedford, MA, USA) to remove suspended solids. They were finally stored in amber bottles at 4 °C until analysis.

Results and discussion

Organic solvent evaporation step

To exchange the solvent before the HPLC analysis, the sedimented phase should be evaporated with a gentle stream of nitrogen gas. Owing to the high volatility of some of the analytes (e.g., Ph), the evaporation step should be performed very carefully. To avoid loss of phenols during solvent evaporation, the evaporation rate should be kept at a minimum [26]. In addition, conversion of phenols into ionized compounds by alkalization of the solution prevents evaporative loss of the analytes [26, 27]. However, the degree of alkalization is critical and must be controlled as insufficient alkalization of the solvent leads to the loss of some of the compounds [27]. On the other hand, certain compounds, such as 2,4-DNP, may be decomposed in strongly alkaline solutions.

In this work, TEA was used to alkalize the settled phase before evaporation. To study the influence of TEA addition on the analyte signal, different amounts of TEA (0, 2, 5, 10, and 20 μL) were added to the standard solution of phenols in CS_2 at 2 mg/L (144 μL standard solution plus 10 μL internal standard solution). The evaporation step was carried out with a gentle stream of nitrogen gas at a rate which evaporated approximately 15 μL of the extract per minute [26]. The residue was dissolved in 25 μL of water–methanol mixture (3:7) and a 20-μL aliquot was injected into the HPLC system for analysis. The results showed that 5 μL of TEA was sufficient to prevent evaporation losses of the analytes during solvent elimination. Higher amount of TEA did not increase the peak heights of the analytes. Figure 1 show chromatograms obtained with and without TEA addition during the evaporation step. As can be seen, addition of TEA to the solvent is necessary before evaporation.

Optimization of the DLLME procedure

To develop a DLLME method for determining phenols in water samples, it is essential to investigate the effects of different parameters involved in extraction performance, such as type and volume of organic solvent, type and volume of dispersive solvent, sample pH, and ionic strength. In this study, all the determinations were based on the relative peak area of the analyte to the internal standard, from the average of three replicate measurements.

The choice of an appropriate solvent is essential for the DLLME method. The extraction solvent has to satisfy the following four requirements: low solubility in water, convenient extraction of the analytes, higher density than water, and peaks that are separated and discernible from those of the analyte when directly injected for chromatographic analysis. On the basis of these considerations, three solvents, i.e., CCl_4 (density 1.58 g/mL), CS_2 (density 1.25 g/mL), and $C_2Cl_3F_3$ (density 1.57 g/mL), were examined to find the best one for the extraction of phenols. To pick up a constant volume of the sedimented phase (43 μL), different volumes of the extraction solvents were added to the sample: 70, 53, and 58 μL of CS_2, CCl_4, and $C_2Cl_3F_3$, respectively, were selected. A series of sample solutions adjusted to pH 2 were studied by using 1.60 mL methanol containing the above-mentioned volumes of the extraction solvents to achieve 43 μL of the settled phase. The results revealed that CS_2 had the highest extraction efficiency in comparison with the other solvents. For this reason, CS_2 was selected as the extraction solvent.

To select a dispersive solvent, the miscibility of the solvent in both water (sample) and the organic solvent had to be considered. Therefore, three common dispersive solvents (i.e., acetone, methanol, and acetonitrile) were investigated in this work. To achieve a constant volume of the sedimented phase (43 μL), the experiments were performed using 1.60 mL of each of the acetone, methanol, and acetonitrile solvents containing 68, 70, and 72 μL of CS_2, respectively. The effects of different dispersive solvents on extraction performance are given in Fig. 2. Obviously, acetone gave the best extraction efficiency for all the compounds studied.

To study the influence of the volume of the organic solvent (CS_2), a constant volume of acetone (2.00 mL) containing different volumes of CS_2 from 80 to 180 μL at 20-μL intervals was investigated. Under these conditions, the volumes of the sedimented phase were 62, 80, 100, 122, 144, and 161 μL, respectively. The results are shown in Fig. 3. The extraction efficiency of all the compounds except PCP and 2-M-4,6-DNP improved with increasing

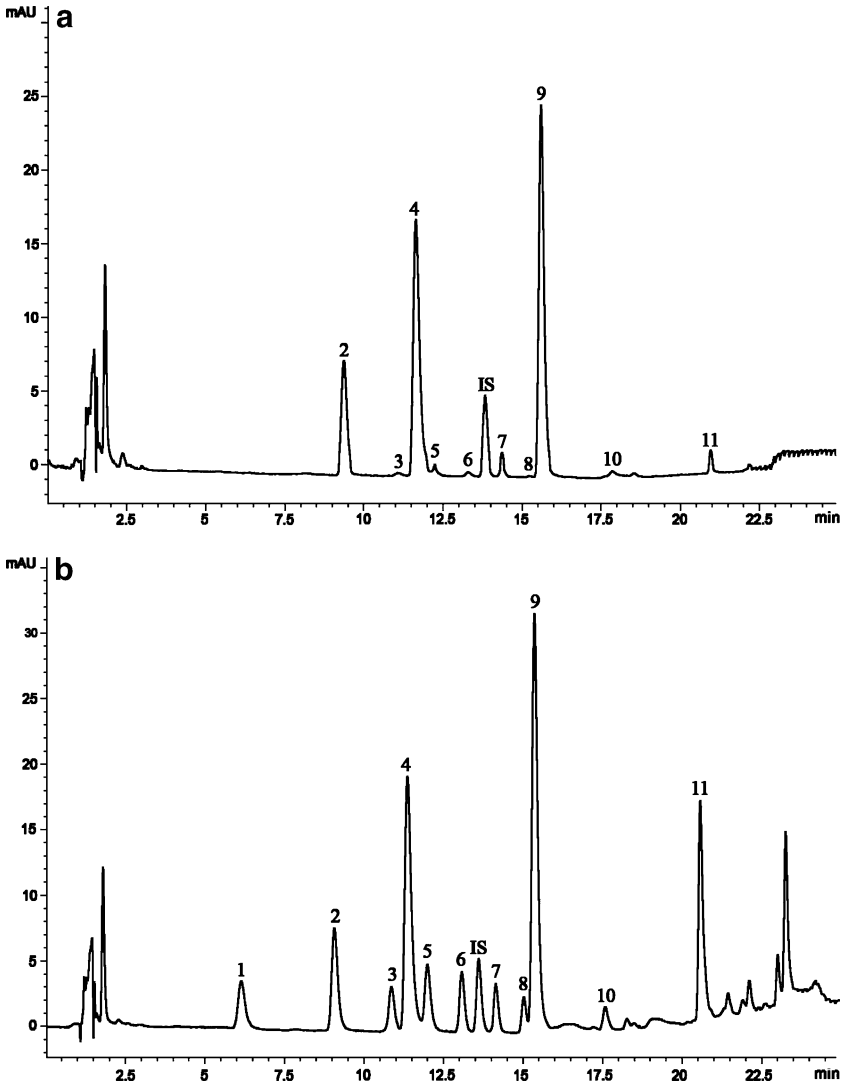

Fig. 1 Chromatograms obtained after evaporation of a standard solution (144 μL standard solution of phenols at 2 mg/L) and reconstitution of the residue in 25 μL of water–methanol mixture (3:7): **a** evaporation without addition of triethylamine (TEA); **b** evaporation after addition of 5 μL of TEA. *IS* internal standard, *1* phenol, *2* 4-nitrophenol (4-NP), *3* 2-chlorophenol (2-CP), *4* 2,4-dinitrophenol (2,4-DNP), *5* 2-nitrophenol (2-NP), *6* 2,4-dimethylphenol (2,4-DMP), *7* 4-chloro-3-methylphenol (4-C-3-MP), *8* 2,4-dichlorophenol (2,4-DCP), *9* 2-methyl-4,6-dinitrophenol (2-M-4,6-DNP), *10* 2,4,6-trichlorophenol (2,4,6-TCP), *11* pentachlorophenol (PCP)

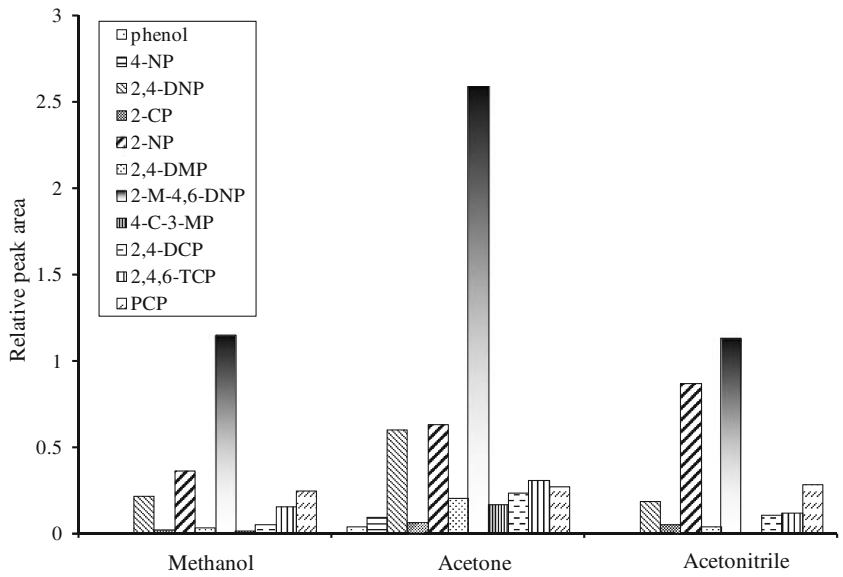

Fig. 2 Effect of different dispersive solvents on the extraction recovery of the phenols. The extraction conditions were as follows: sample volume, 5.0 mL; concentration of analytes, 60 μg/L; sample pH, 2.0; dispersive solvent volume, 1.60 mL; extraction solvent, CS_2; no NaCl added; room temperature

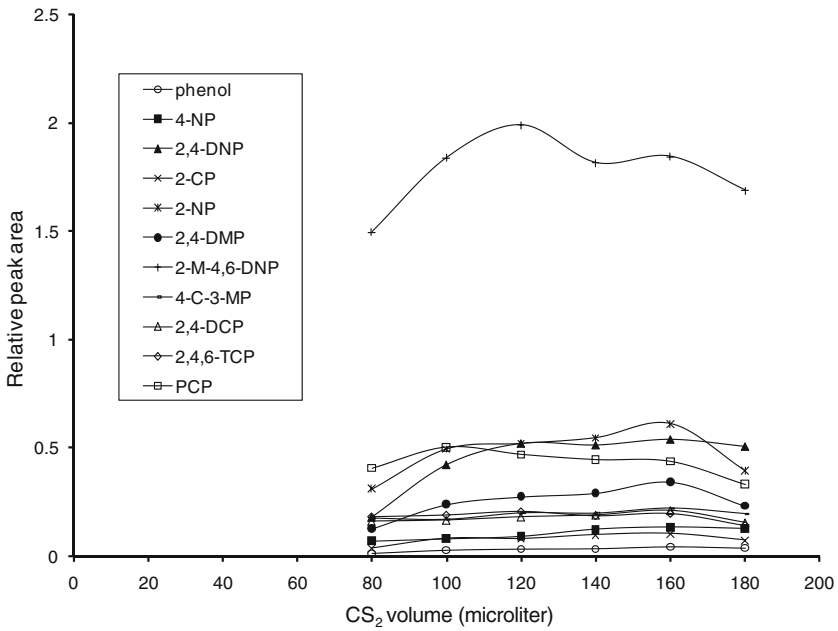

Fig. 3 Effect of the extraction solvent (CS_2) volume on the recovery of the phenols. The extraction conditions were as follows: sample volume, 5.0 mL; concentration of analytes, 60 μg/L; sample pH, 2.0; dispersive solvent (acetone) volume, 2.00 mL; no NaCl added; room temperature

volume of the extractant up to 160 μL. A small decrease in efficiency was observed above 180 μL. This is probably due to increasing droplet size as a decrease in the ratio of the dispersive to the extraction solvent volumes. For PCP and 2-M-4,6-DNP, maximum extraction performance was observed using 100 and 120 μL CS_2, respectively. On the basis of the results, 160 μL CS_2 was used as the extraction solvent in subsequent experiments.

The effect of the quantity of the dispersive solvent on the extraction efficiency was investigated over the range 1.50–3.00 mL. Since variation of acetone volume changes the volume of the settled phase, the volumes of acetone and CS_2 have to be changed simultaneously to recover a constant volume of the settled phase (144 μL). Several experiments were performed using different volumes of acetone: 1.50, 2.00, 2.50, and 3.00 mL containing 156, 160, 165, and 167 μL CS_2, respectively. The results reported in Fig. 4 show that using 2.50 mL acetone as the dispersive solvent yielded the best extraction efficiency.

The addition of salt sometimes improves recovery when microextraction methods such as SDME and DLLME are used [18, 28, 29]. To study the influence of salt addition, different concentrations of NaCl from 0 to 5% (w/v) were used. No significant effect was observed on the extraction

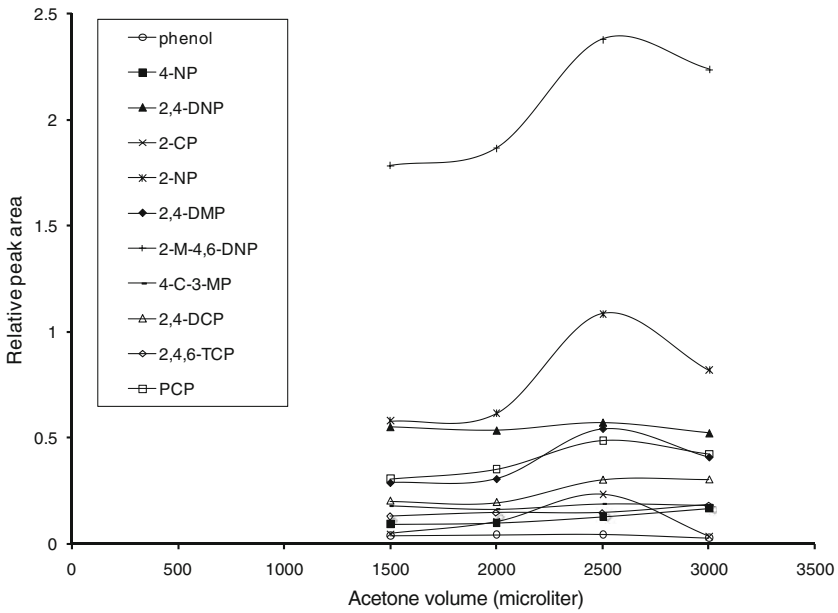

Fig. 4 Effect of the dispersive solvent (acetone) volume on the recovery of the phenols. The extraction conditions were as follows: sample volume, 5.0 mL; concentration of analytes, 60 μg/L; sample pH, 2.0; extraction solvent, CS_2; no NaCl added; room temperature

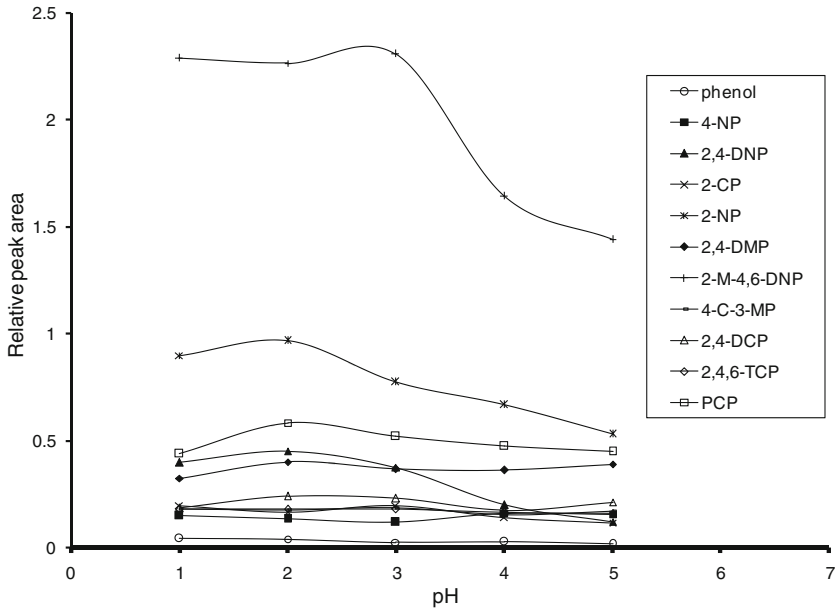

Fig. 5 Effect of the sample pH on the recovery of the phenols. The extraction conditions were as follows: sample volume, 5.0 mL; concentration of analytes, 60 μg/L; dispersive solvent (acetone) volume, 2.50 mL; extraction solvent, 165 μL CS_2; no NaCl added; room temperature

efficiency of any of the phenolic compounds and the extraction recovery was almost constant. For this reason, no salt was added in subsequent experiments.

The ionic or molecular form of the analytes largely influences the affinity of a compound for the extraction solvent. It is important to control the pH of the extraction medium both to enhance the affinity of each compound for the solvent and to improve extraction. To increase the extraction recovery of phenols in conventional sample preparation methods, such as liquid—liquid extraction, solid-phase extraction, solid-phase microextraction, and SDME [6, 30, 31], it is necessary to acidify the sample. For this reason, the extraction behavior of phenols was studied at various pH levels (1–5); the results are shown in Fig. 5. The best response for the majority of the target compounds was obtained at pH 2.0.

Quantitative aspects

The method was evaluated for the reproducibility, linear range, enrichment factor, and limit of detection. The results are summarized in Table 1. The reproducibility of the method, using the optimal experimental conditions, was determined by analyzing five replicate HPLC water samples

Table 1 Analytical figures of merit for the dispersive liquid—liquid microextraction (DLLME) high-performance liquid chromatography—diode-array detection (HPLC-DAD) of phenols

Compound	Detection wavelength (nm)	Linear range (μg/L)	r^2	LOD (μg/L)	Precision[a]	EF
Ph	200	5–200	0.9967	1.3	14.8	30
4-NP	302	0.5–200	0.9990	0.3	6.7	37
2-CP	200	0.5–100	0.9961	0.2	6.2	60
2,4-DNP	285	0.4–500	0.9994	0.2	6.4	102
2-NP	285	0.5–500	0.9958	0.4	16.6	97
2,4-DMP	200	0.1–200	0.9962	0.03	4.3	123
4-C-3-MP	200	0.1–200	0.9992	0.04	4.3	151
2,4-DCP	230	0.4–200	0.9972	0.1	5.4	181
2-M-4,6-DNP	270	0.4–200	0.9997	0.1	2.6	256
2,4,6-TCP	230	1–200	0.9975	0.4	5.3	303
PCP	210	0.1–100	0.9964	0.01	7.3	373

LOD limit of detection, *EF* enrichment factor, *Ph* phenol, *4-NP* 4-nitrophenol, *2-CP* 2-chlorophenol, *2,4-DNP* 2,4-dinitrophenol, *2-NP* 2-nitrophenol, *2,4-DMP* 2,4-dimethylphenol, *4-C-3-MP* 4-chloro-3-methylphenol, *2,4-DCP* 2,4-dichlorophenol, *2-M-4,6-DNP* 2-methyl-4,6-dinitrophenol, *2,4,6-TCP* 2,4,6-trichlorophenol, *PCP* pentachlorophenol

[a] Precision expressed as percentage relative standard deviation (RSD%; $n=5$)

Table 2 Comparison of the proposed DLLME HPLC-DAD with other extraction methods for the determination of phenols

Method	LOD (μg/L)	Precision[a]	Derivatization reagent	Sample preparation time (min)	Real sample	Reference
SBSE-TD-GC-MS	0.1–0.4	6–27	Acetic anhydride	50	Groundwater and lake water	[32]
LGLME-CE-DAD	0.5–10	2.7–7.6	–	10	Industrial effluent	[8]
SPME-GC-MS	0.052–9.1	3.3–20	–	40	Underground and surface water	[30]
SPE-CE-DAD	28–399	6.7–12.3	–	> 20	Wastewater	[33]
SME-GC-MS	0.005–0.022	< 10	Acetic anhydride	25	River water	[34]
SPME-HPLC-UVD	0.25–3.67	1.52–6.38	–	30	River water and wastewater	[35]
SPE-HPLC-IFD[f]	0.0012–66.585	–	Sodium 1-naphthalenesulfonate	–	Wastewater	[36]
SDME-GC-MS	0.004–0.061	4.8–12	*N*,*O*-Bis(trimethylsilyl) acetamide	20	River water	[31]
LLE-GC-MS (EPA method 625)	1.5–42	–	Pentafluorobenzyl bromide	> 60	Municipal and industrial wastewater	[4]
This work	0.01–1.3	2.6–16.6	–	15	Industrial wastewater	–

SBSE stir bar sorptive extraction, *TD* thermal desorption, *GC* gas chromatography, *MS* mass spectrometry, *LGLME* liquid–gas–liquid microextraction, *CE* capillary electrophoresis, *DAD* diode-array detection, *SPME* solid-phase microextraction, *SPE* solid-phase extraction, *SME* solvent microextraction, *HPLC* high-performance liquid chromatography, *UVD* UV detection, *IFD* indirect fluorophotometric detection, *SDME* single-drop microextraction, *LLE* liquid—liquid extraction

[a] Precision expressed as RSD%

spiked with 10 μg/L of the analytes. The method was reproducible at a precision between 2.6 and 7.3% ralative standard deviation, except for 14.8% for Ph and 16.6% for 2-NP. Ph and 2-NP are very volatile and their worse reproducibility may be due to the loss of these analytes during the evaporation step.

The enrichment factor was calculated as the ratio of the analyte's ultimate concentration in the extractant after extraction to its initial concentration in the aqueous solution. The enrichment factors were obtained by three replicate extractions of water samples. The results indicate that the enrichment factors lie between 30 and 373.

To test the linearity of the calibration curves, various concentrations of the phenols ranging from 0.1 to 500 μg/L were analyzed. As shown in Table 1, a linear relationship was obtained in the specified range for all the phenols studied, with squared correlation coefficients (r^2) between 0.9958 and 0.9997. The limits of detection, calculated at a

Table 3 Analysis results of wastewater samples

Compound	Sample 1		Sample 2		Sample 3		Sample 4	
	Found (μg/L)	R^a	Found (μg/L)	R^a	Found (μg/L)	R^a	Found (μg/L)	R^a
Ph	15.5	83±14	ND	88±13	12.9	102±15	13.5	99±15
4-NP	6.1	68±10	ND	89±12	12.1	58±12	ND	95±7
2-CP	2.9	100±6	ND	98±6	ND	87±6	ND	97±9
2,4-DNP	6.0	83±7	ND	98±6	1.1	100±6	2.0	78±7
2-NP	2.8	65±17	ND	96±19	5.7	62±19	4.3	95±17
2,4-DMP	ND	79±8	ND	81±8	ND	89±8	3.3	87±9
4-C-3-MP	ND	101±8	ND	102±4	ND	94±4	ND	108±4
2,4-DCP	ND	88±6	ND	104±7	ND	96±7	ND	107±10
2-M-4,6-DNP	1.6	99±5	ND	100±5	1.6	85±5	0.84	99±6
2,4,6-TCP	ND	100±10	ND	99±5	ND	106±5	1.1	65±9
PCP	ND	91±8	ND	83±8	ND	85±8	ND	86±7

ND not detected

[a] Relative recovery (%) ± RSD% (n=3)

signal-to-noise ratio of 3 based on peak-to-peak noise, ranged between 0.01 and 1.3 μg/L.

Compared with other relevant methods for the analysis of phenols (Table 2), the proposed method exhibits adequately low detection limits and good precision, and low quantities of the solvent and the sample are consumed.

Wastewater samples

The influence of the matrix on the extraction efficiency of the method was evaluated using four wastewater samples (Table 3). The standard addition technique (four data points) was used for the determination of phenols in spiked and nonspiked samples. The analytes were added to the

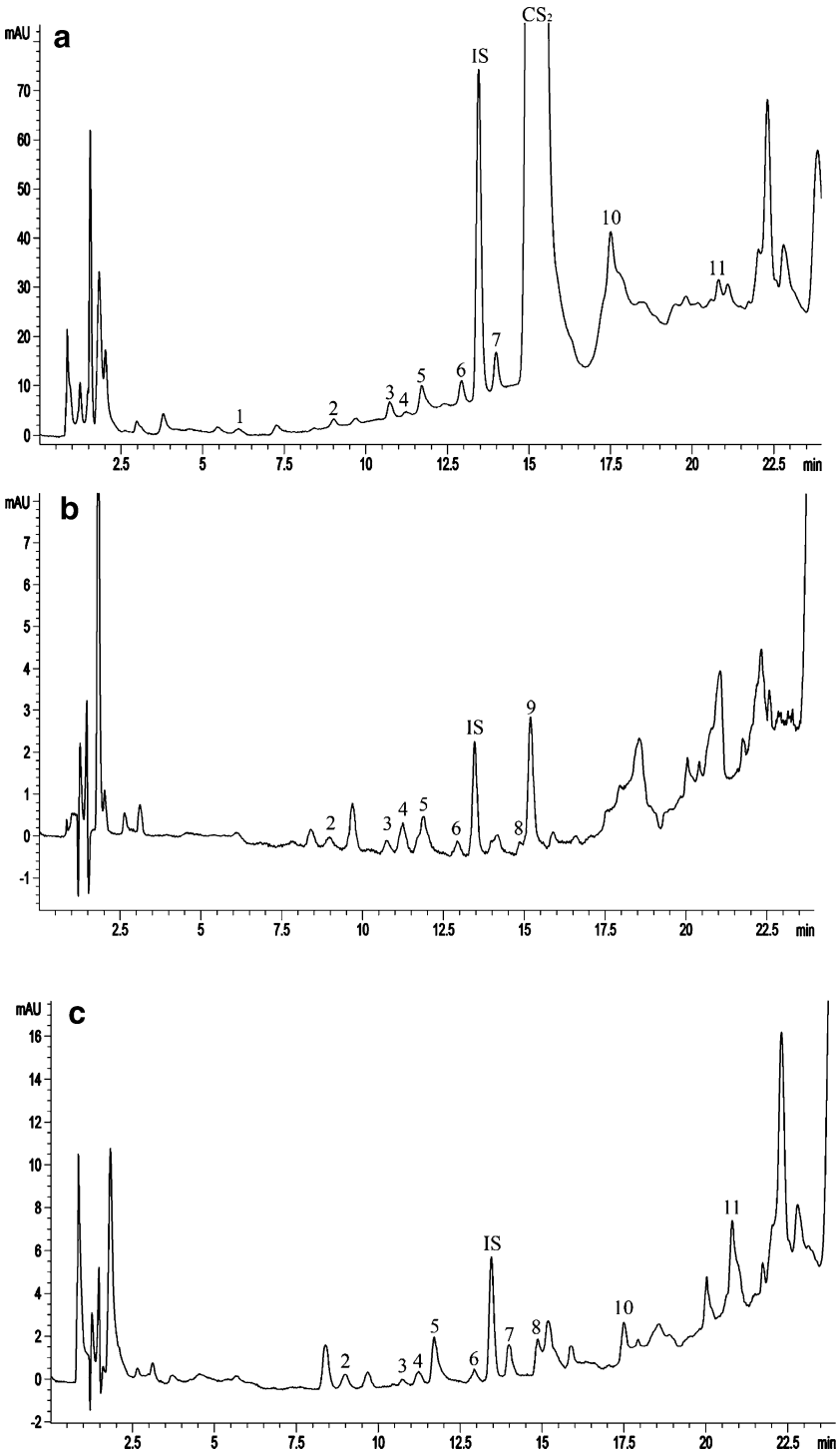

Fig. 6 Chromatograms of phenols obtained after dispersive liquid—liquid microextraction of spiked wastewater sample (sample 2) at a concentration 5 μg/L. Detection wavelength **a** 200 nm, **b** 270 nm, and **c** 230 nm. For peak assignment, see Fig. 1

samples at four concentrations (0, 5, 10, and 20 μg/L). The correlation coefficients of the calibration plots were higher than 0.99. The linearity of the plots indicates that the method is sufficiently precise. All compounds were detected in the samples except for 4-C-3-MP, 2,4-DCP, and PCP. The results are presented in Table 3.

The relative recoveries were calculated on the basis of the ratios of the peak areas of the added analytes in real samples and the peak areas of analytes in pure water samples spiked with the same amounts of the analytes. The spiked samples (at 10 μg/L) were analyzed in triplicate and the relative recoveries along with relative standard deviations were calculated and are summarized in Table 3. The relative recoveries for most of the analytes in the four samples were more than 80%, indicating that the influence of the matrix was not significant for wastewater analysis. Similar to ultrapure water analysis (Table 1), the relative standard deviations were lower than 10% for most of the analytes.

Figure 6 shows the chromatograms obtained after DLLME of sample 2 spiked with a standard solution (5 μg/L) of phenols at three detection wavelengths (200, 270, and 230 nm). At 200 nm, owing to the presence of a trace amount of CS_2, 2,4-DCP and 2-M-4,6-DNP were coeluted with CS_2. However, as can be seen in the chromatograms, at other detection wavelengths, CS_2 does not interfere with quantification of these two compounds.

Conclusion

A method based on DLLME for the determination of 11 priority pollutant phenols in wastewater samples by HPLC—diode-array detection has been developed. Analysis of phenols at parts per billion levels in wastewater is challenging owing to matrix effects and the range of interferences likely to be present. DLLME is a very fast and inexpensive sample preparation technique compared with other methods such as solid-phase extraction and solid-phase microextraction, which are routinely used for sample preparation of highly polluted water samples. This work indicates that extraction of phenolic compounds from wastewater samples can be achieved by a DLLME method. The analytical performance of the proposed method was validated and the method was successfully used for the determination of these compounds in industrial wastewater samples.

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