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Bio-sorption based dispersive liquid–liquid microextraction for the highly efficient enrichment of trace-level bisphenol A from water samples prior to its determination by HPLC

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ABSTRACT

In this study, biosorption based dispersive liquid liquid microextraction (Bio-DLLME) has been developed as a new method for the extraction of bisphenol A (BPA) from water samples. In this technique, the BPA is extracted into a stable cloudy phase. The colloidal phase is composed of micro-particles made from rhaminolipid biosurfactant and methanol, which dispersed in the water samples and facilitated the breakdown of analyte matrix bonds and provided high extraction yields. Rhaminolipid biosurfactants form a thin molecular interfacial film. This layer is formed between donor and recipient phase. This molecular layer, lowers the interfacial tension between immiscible phases (aqueous solution: colloidal particles) and allow dissimilar phases to mix and interact more easily. So the equilibrium state is achieved quickly and, therefore, the extraction time is very short. The attraction of the proposed method is that the extraction is fast, simple and can be done without toxic organic solvents. Also bioaggregates have several advantages such as higher environmental compatibility and biodegradability. Experimental parameters affecting the extraction efficiency were studied and optimized. Under the optimum conditions, relative recoveries of BPA were in the ranges of 98–103.3%. The calibration plot is linear in the range between 1 and 1000 $\mu g\,L^{-1}$ ($R^2 = 0.998$), and the relative standard deviation (RSD, for n = 6) is 3.24%.

1. Introduction

In recent years, sample preparation techniques have been intensely investigated in order to improve the isolation and preconcentration steps of the analytical procedures [1–4]. The ideal sample preparation technique should be simple, rapid, inexpensive and safe to environment. In this context, rapidity, simplicity in operation and safe to environment can be considered as key trends in this evolution [5,6]. The present work is mainly focused on the development of new techniques and the application of Eco-friendly materials (rhaminolipid biosurfactant) in order to anlyte extraction. In this research, the extension of the contact surface between the two phases (organic phase and aqueous phase) can greatly reduce the extraction time. This is due to the lower surface tension in two phases (donor phase and recipient phase). Long sample preparation times are obviously disadvantageous and multi-step procedures are prone to loss of analytes [7,8]. Also, analytical chemists look to reduce the amounts of solvents and chemicals used in analytical experiments, so miniaturization of conventional extraction methods to minimize analysis time and level of consumption of chemicals is recommended [9].

Dispersive liquid liquid microextraction (DLLME) is one of the effective microextraction techniques. The extraction is carried out between the sample and a cloud of fine extractant drops formed when the mixture of extraction and disperser solvents is injected in the aqueous sample. The contact surface between phases is widely increased reducing the extraction time and improving the enrichment factor [10–14]. DLLME is a miniaturized LLE which uses microliter volumes of extraction solvents. It is based on equilibrium distribution of the analytes between sample solution and extraction solvent [15,16]. Because DLLME is simple to perform, rapid, and low cost, and results in high recovery and enrichment it is widely used for trace analysis. Commonly, acetonitrile, acetone and methanol have been used as disperser solvents in DLLME procedures, to form a cloudy phase and effectively extract the analyte via the high contact surface areas generated [17,18].

Although DLLME technique has been successfully used for the analysis of a wide range of organic and inorganic compounds [19,20], but this method uses toxic and hazardous organic solvents as the microextraction solvent [21]. For this reason, dispersive liquid–liquid microextraction modified by our group. The pre-

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sented method explores a novel combination of DLLME with bioaggregates based microextraction technique as a high performance and powerful preconcentration method which is based on biosorption phenomenon [22], and termed biosorption based dispersive liquid–liquid microextraction (Bio–DLLME). The method not only possesses all of the advantages of routine DLLME; but it also, leads to more stable cloudy states for performing effective extraction. This feature was attributed to the fact that biosurfactants are active at extreme temperatures, pH and salinity as well [23–25]. According to the procedure, a colloidal mixture containing appropriate amounts of the rhaminolipid biosufractant (microextraction solvent) and methanol (disperser solvent), is injected into the sample. Then the solution was centrifuged to accelerate the separation of the colloidal phase from the bulk solution. Finally, the colloidal phase withdrawn with microsyrange and injected into LC system. The advantage of Bio-DLLME is the preferable use of rhaminolipid biosurfactant as the microextraction solvent in the colloidal solution, which is benign to the environment, as compared with the organic solvents still used in other preconcentration procedures. Moreover, biosurfactants offers the advantages such as environmentally friendly and biodegradable [23].

2. Experimental

2.1. Chemical and reagents

All chemicals were of analytical reagent grade. Methanol, acetone and isopropanol were purchased from Merck (Darmstadt, Germany). Bisphenol A (BPA), and R-95 HPLC grade monorhamnolipid biosurfactant purchased from (Sigma-Aldrich, USA). Working standard solutions were freshly prepared by diluting the standard solution of the analyte with ultra-pure water to the required concentration. Proper amounts of BPA were dissolved in methanol to obtain stock solution of the analyte with a concentration of 250 mg L^{-1}.

2.2. Instrumentation

The HPLC system equipped with a manual injector 20 μL sample loop and a UV–vis detector (smart line 2500) which was set at 224 nm wavelength for the detection and quantification of analyte. A reversed-phase VP-ODS C18 column (250 mm × 4.6 mm i.d., particle size 5 μm) (Shimadzu, Japan) was used for the analysis of bisphenol A at 25 °C. Methanol: water (55:45, v/v) was used as the mobile phase at a flow rate 1.0 mL min^{-1}. The pH measurements were carried out with a pH meter (Metrohm, Switzerland). Centrifuge (Beckman, USA), was used for separation of the phases.

2.3. Sample preparation

Real samples were taken from the ground and river water and filtered through 0.45 μm micropore membranes to remove any solids and impurities and analyzed by the Bio-DLLME. The data in Table 1 show that the relative recoveries of BPA were in the ranges of 98%–103.3%, demonstrating that the ground and river waters matrices had not effect on the Bio-DLLME.

2.4. General procedure for Bio-DLLME

The Bio-DLLME procedure is fast and simple. Under the optimum conditions of Bio-DLLME, 10.0 mL of water samples containing BPA was placed in a 15 mL conical bottom glass tube. 250 μL of methanol (disperser solvent) containing 40 mg rhaminolipid biosurfactant (extraction solvent) was injected into the water samples by using a 1.0 mL syringe. Subsequently, the mixture was vortexed for 40 s at the highest speed and then centrifugated at 3000 rpm for 5 min to speed up the complete separation of the dispersed micro assemblies. A cloudy solution (methanol/rhaminolipid biosurfactant) was formed in the tube. Colloidal phase, was withdrawn using a microsyringe and it was subject to LC analysis.

2.5. Calculation of enrichment factor and extraction recovery

The enrichment factor (EF) for the target analyte was calculated according to the following equation:

$$EF = \frac{C_{ex}}{C_o} \quad (1)$$

where C_{ex} is final concentration of the analyte in acceptor phase, and C_o is the initial analyte concentration in the donor phase.

C_{ex} is obtained by comparing the peak areas obtained from direct injection of standard solution of the BPA in the extraction solvent with those obtained by applying the proposed method on aqueous sample solutions containing the analyte. Extraction recovery (ER) is defined as the percentage of total analyte (C_o)that is extracted into the colloidal phase (C_{ex}):

$$ER = \frac{C_{ex}}{C_o} \times 100 = EF \times \frac{V_a}{V_s} \times 100 \quad (2)$$

where V_a is the acceptor phase volume, and V_s is the sample volume.

3. Result and discussion

In order to select the optimum Bio-DLLME conditions for the determination of BPA, a procedure was required to optimize the different parameters that affect the Bio-DLLME extraction process. In this study, parameters affecting microextraction such as pH, ionic strength, vortex extraction time and centrifuging conditions, amount microextraction solvent and type and volume of disperser solvent were optimized in order to minimize analysis time and to obtain maximum extraction efficiency.

3.1. Optimization of operation conditions

3.1.1. Effect of the pH

Enrichment factor is governed by the affinity of the analyte for suitable solubility in the acceptor phase. For compounds with acidic

Table 1
The results of the quantitative analysis of BPA in natural samples by Bio-DLLME.[a]

Real sample	Concentration BPA (μg L^{-1})	Added BPA (μg L^{-1})	Found (μg L^{-1}) (±RSD[c]) (n = 4)	Relative recovery (%)
Ground water	ND[b]	1.0	1.02(±5.28)	102
		3.0	2.98(±5.64)	99.3
River water	ND[b]	1.0	0.98(±4.69)	98
		3.0	3.1(±6.18)	103.3

[a] Extraction conditions: Extraction method, vortex; amount of microextraction solvent, 40 mg of rhaminolipid biosurfactant; extraction time, 40 s; disperser solvent, 250 μL of methanol; pH value of sample solution, 3.
[b] Not detected.
[c] Relative standard deviation.

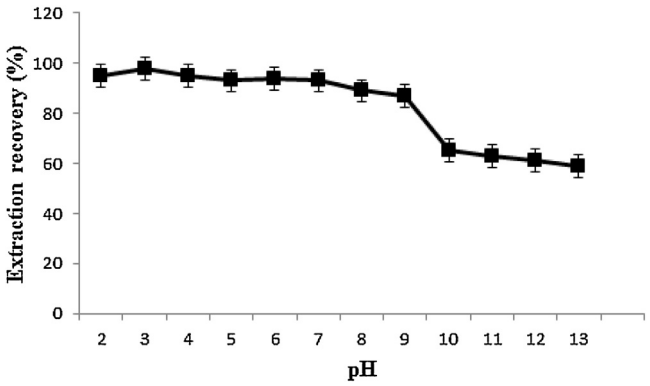

Fig. 1. Effect of pH value of sample solution on the extraction recovery; microextraction solvent: rhaminolipid biosurfactant, disperser solvent: methanol, mobile phase: methanol: water (55:45, v/v), VP-ODS C18 column, extraction time 40 s, flow rate 1 mL min^{-1}.

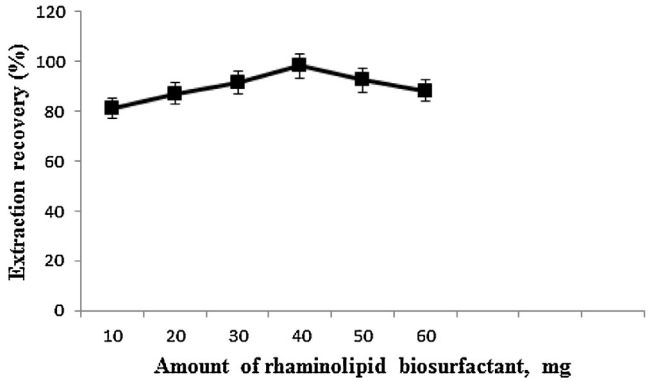

Fig. 2. Effect of amount of microextraction solvent on the extraction recovery; disperser solvent: methanol, mobile phase: methanol: water (55:45, v/v), VP-ODS C18 column, extraction time 40 s, flow rate 1 mL min^{-1}.

and basic functional groups, the pH of the liquid phase determines the chemical species present (cationic, anionic or neutral) and thus the distribution ratio of the analyte between the two phases. In this experiment, the influence of pH was studied over the range of 2.0–13.0. The results are shown in Fig. 1, which reveals that the maximum extraction efficiency of BPA can be achieved at pH 2.0–9.0, while the lowest recoveries were obtained at pH > 10. It was found that the extraction performance of BPA at the range of 2.0–9.0 had no big differences. When the pH was in the range of 2.0–9.0, BPA exists in a molecular state (pKa_{BPA} = 9. 73). While at (pH □ pka), BPA will exist in the ionized forms, which does not benefit for extraction. Based on the above mentioned experimental results, the pH of working sample was adjusted to 3.0 in the following experiments.

3.1.2. *Effect of ionic strength*

Usually the presence of a salt in aqueous solution affects the solubility of organic solutes. The addition of salt has a dual effect on extraction efficiency. Ionic strength may enhance the extraction of the analyte by a salting out effect and extraction time is reduced. But in the case of extraction method, the extraction recovery of BPA decreases with increasing ionic strength. The ionic strength limits the extraction due to increase in aqueous solution viscosity which leads to a decrease in the analyte mass transfer from the aqueous solution into the acceptor phase. Taking the above reason into account, salt was not added.

3.1.3. *Investigation of vortex extraction time and centrifuging conditions*

Optimal vortex extraction time and centrifuging conditions are necessary to efficient extraction, and achieve an easy and efficient phase separation and preconcentration. It is known that generally the dispersion of the colloidal phase into the aqueous sample can depend on the rotational speed and vortex time. Extraction time in Bio-DLLME is defined as the interval of time between the instant of injection of the mixture of microextraction solvent (rhaminolipid biosurfactanr) and disperser solvent (methanol) into aqueous phase, under vortex stirring, before centrifugation. The effect of the vortex extraction time was investigated in the range of 0–160 s at highest rotational speed (2000 rpm). It was found that extending the extraction time to more than 40 s had no significant effect on the extraction recovery. The equilibrium state could be achieved in 40 s and shorter time was not enough for the whole system to achieve the equilibrium. For this reason, 40 s was selected as the optimum extraction time. The effect of time and speed of centrifuging were examined in the ranges of 1–10 min and 1000–4000 rpm, respectively. Time and speed of centrifuging had a little effect on the extraction efficiency because after mixing the colloidal phase with aqueous solution the equilibrium status was achieved in a few seconds due to the large contact surface between the micro assemblies of the extraction solvent and sample. In fact, centrifugation is only used to help phase separation. Thus, time and speed of centrifuging at 5 min and 3000 rpm, respectively, were chosen to ensure that the phase separation be complete.

3.1.4. *Effect of the amount of microextraction solvent*

The microextraction solvent in Bio-DLLME has to meet several requirements: low solubility in water and low volatility. Most of the halogenated solvents applied in DLLME possess all of above properties, but these solvents are highly toxic and their use is not. It was observed that the extraction efficiency of the Bio-DLLME procedure was significantly affected by the amount of extracting solvent. To examine the effect of the amount of microextraction solvent, solutions containing different amount of rhaminolipid biosurfactant were subjected to the same Bio-DLLME procedure. The experimental conditions were fixed and included the use of 500 μL of methanol (as disperser solvent) containing different amount (i.e., 10.0, 20.0, 30.0, 40.0, 50.0 and 60.0 mg) of rhaminolipid biosurfactant. As the concentration of rhaminolipid biosurfactant increased from 10.0 to 60.0 mg (in 500 μL of methanol), the volume of the colloidal phase increased from 50.0 to 150 μL, resulting in a decrease on enrichment factor. Therefore, the optimal amount of microextraction solvent should ensure both high enrichment factor and enough volume of the colloidal phase for the subsequent analysis after centrifugation. As can be seen in Fig. 2, the extraction recovery of the BPA increased with the amount of rhaminolipid biosurfactant up to 40 mg, and then decreased for higher values. Thus, 40 mg rhaminolipid biosurfactant was selected as optimum. Therefore, at optimum volume of microextraction solvent, high enrichment factor and good recovery are obtained.

3.1.5. *Influence of the type and volume of disperser solvent*

The disperser solvent must be miscible in extraction solvent and also sample solution (aqueous phase). In the current study, three solvents including methanol, acetone and isopropanol were evaluated. A series of sample solutions was studied by using 500 μL of each disperser solvent containing 40 mg of rhaminolipid biosurfactant as microextraction solvent. The maximum extraction recovery was obtained by using methanol as a disperser solvent. That is due to its higher compatibility of methanol with an aqueous solution than the other solvents. During the microextraction process, disperser solvent volume is an essential factor which can influence the occurrence of the cloudy state and also determine the enrichment performance. Also disperser solvent volume had a significant effect the dispersion degree of the extracting solvent in aqueous phase

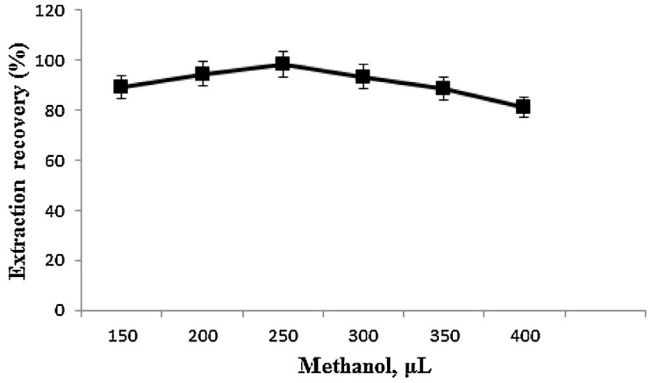

Fig. 3. Effect of disperser solvent volume on the extraction recovery; mobile phase: microextraction solvent: rhaminolipid biosurfactant, methanol: water (55:45, v/v), VP-ODS C18 column, extraction time 40 s, flow rate 1 mL min^{-1}.

and, subsequently, the extraction efficiency. The effect of mehanol volume on the extraction of BPA was examined in the range of 150–400 μL, but varying the volume of methanol causes changes in the volume of the colloidal phase. To avoid this problem and in order to attain a constant volume of colloidal phase, the volume of methanol and rhaminolipid biosurfactant were changed simultaneously. The experimental conditions were fixed and included the use of different volumes of methanol: 150, 200, 250, 300, 350 and 400 μL containing 6.0, 8.0, 10.0, 12.0, 14.0 and 16.0 mg of rhaminolipid biosurfactant, respectively. The results were exhibited in Fig. 3. As can be seen, extraction recovery of BPA increased with the methanol volume (up to 250 μL), and then decreased when the volume was continuously increased up to 400 μL. Therefore, in all subsequent experiments, 250 μL methanol was used as the disperser solvent. For lower volumes, the cloudy suspension could not be formed because the small amount of methanol could not disperse the extraction solvent properly as tiny droplets in the aqueous solution. On the other hand, using higher volumes, both the volume of the colloidal phase and the extraction efficiency of the target analyte decreased, may be due to the increase of the solubility of the analyte and extraction solvent in the sample solution.

3.2. Comparison of proposed Bio-DLLME with the other methods

A comparison of our method with those reported for the BPA preconcentration with a chromatography separation system demonstrated the superior performance of this newly-designed method (Table 2). The experimental results indicated that the lower extraction time, good linearity and repeatability of the proposed method will make it a competitive and viable alternative of the routine methods and have a good perspective in the future. Compared with conventional DLLME, rhaminolipid biosurfactant is generally considered to be more environmentally benign than organic solvents. In this work, rhaminolipid biosurfactant, rather than hazardous organic solvents, is used as the extraction solvent, which is environmentally friendly and meets the principles of green analytical chemistry. In comparison with LPME, SBSE SPME and DLLME, the extraction time for Bio-LLME is greatly shortened since the extraction can reach equilibrium extremely quickly due to the large surface area between the bioaggregates and the aqueous sample solution. Bio-DLLME method is a simple, rapid and environmentally friendly technique that can be applied to the extraction of organic compounds from the complex matrix with satisfactory results.

Table 3
Quantitative characteristic of present method for the analysis of BPA.

LDR[a] (μg L^{-1})	r^2[b]	LOD[c] (μg L^{-1})	RSD%	EF ± SD[d]
1–1000	0.998	0.33	3.24	183± 2

[a] Linear dynamic range.
[b] Square of correlation coefficient.
[c] Limit of detection, S/N = 3.
[d] Enrichment factor ±standard deviation (n = 3).

Table 4
Calibration curves and detection limit of bisphenol A in river and ground water samples.

Analyte	Real sample	Regression equation	LOD[a] (μg L^{-1})
Bisphenol A	Ground water	Y = 714.8X + 21.81	2.7
	River water	Y = 938.1X + 31.4	0.33

[a] Limite of detection (signal/noise = 3).

3.3. Quantitative aspects

Repeatability, linearity, correlation coefficient, enrichment factor and detection limit were investigated under optimized experimental conditions. The results are presented in Tables 3 and 4. Linearity was examined in the range 1–1000 μg L^{-1} for BPA. Good linearity was exhibited; values of r^2 equal or exceed 0.998. The relative standard deviation (RSD) was 3.24%. The high enrichment factor (183) can be attributed to accessible sites to the adsorption of the analyte that cause to improve the extraction efficiency. The limits of detection, which was calculated using a signal-to-noise ratio of 3, is 0.33 μg L^{-1}. Fig. 4a–d show the chromatograms of (a) standard solution of BPA in methanol; (b) river water before spiking; (c) and after spiking with 10 μg L^{-1} of BPA; (d) ground water after spiking with 10 μg L^{-1} of BPA using Bio-DLLME method combined with HPLC-UV under optimum conditions. As can be seen, no significant interference peaks were found at the retention position of cholesterol.

3.4. Matrix effect

Owing to the complexity of environmental samples, effects of the sample matrix on the quantification of the target analytes (effect on the chromatographic response) are very important. The combined effect of all components of the sample matrix different from the target analyte can influence the chromatographic sig-

Table 2
Comparison of Bio-DLLME with other methods.

Method	LOD[b] (μg L^{-1})	LRD[c] (μg L^{-1})	RSD[d] (%)	Extraction time (min)	Ref.
LPME	0.002	0.01–10	3.2–8.9	90	[26]
SBSE[a]	0.12	1–10	–	60	[27]
SPME	0.9	10–500	22	20	[28]
DLLME	0.07	0.5–100	6	<3	[29]
Bio-DLLME	0.33	1–1000	3.24	<1	This work

[a] Concentration units are ng L^{-1}, ng L^{-1} – μg L^{-1}, respectively.
[b] Limit of detection (signal/noise = 3).
[c] Linear dynamic range.
[d] Relative standard deviation (n = 6).

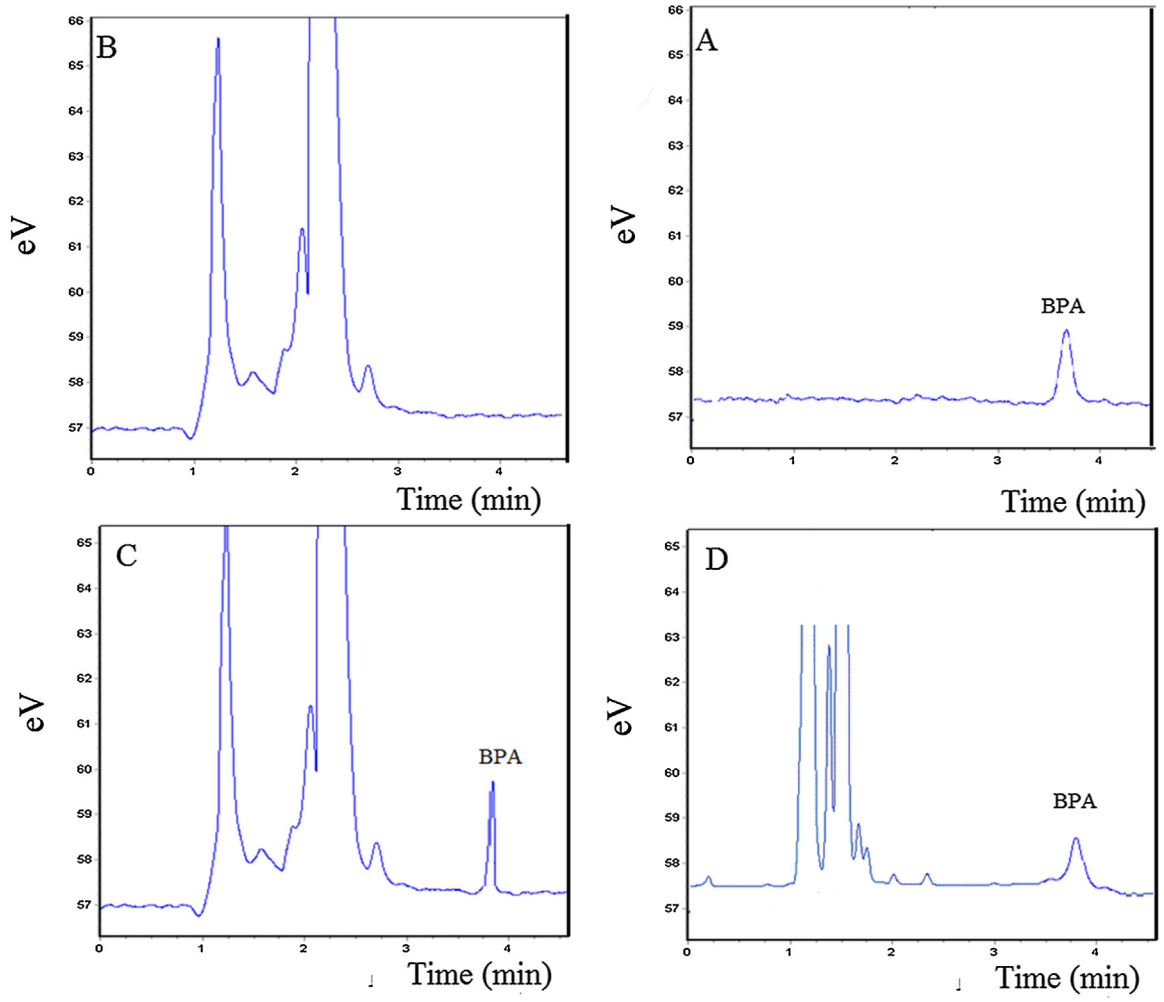

Fig. 4. Chromatograms of (a) standard solution of BPA in methanol; (b) river water before spiking; (c) and after spiking with 10 μg L^{-1} of BPA; (d) ground water after spiking with 10 μg L^{-1} of BPA using Bio-DLLME method combined with HPLC-UV under optimum conditions.

nal, making it decrease or even increase. The matrix suppression effect can lead to a high quality peak area: strong analyte signals and weak or negligible matrix background peaks. The sample matrix can cause an enhancement in the observed chromatographies response for analytes in a matrix extract compared with the same concentration in a matrix-free solution. However, DLLME is not well compatible for extraction of analytes from complex matrix sample, because the interferences from matrix co-extractives are often present. For that reason, the matrix effect evaluated based on an established procedure [30], with slight modification. This method consists of two stages: firstly, extraction from a donor phase in the colloidal phase (bioaggregate), and secondly, back extraction from the colloidal phase into an aqueous acceptor phase. In the first step, by adjusting the pH value for the aqueous sample in acidic region (the donor solution), the analyte (BPA) was extracted into the colloidal phase (50 μL). In the second step, analyte was simply back-extracted into an alkali acceptor solution.

In short: A 5 mL donor phase solution (pH = 3) containing 5 μg L^{-1} of BPA was placed in a 10 mL vial. Then colloidal phase (50 μL) was injected into the water sample by a 100 μL syringe. The mixture was stirred (40 s, 2000 rpm) to favour BPA extraction and then centrifuged at 3000 rpm for 5 min to accelerate the complete separation of the colloidal phase. In the next step, the colloidal phase was transferred into another glass test tube, and 100 μL of the aqueous extracting solution (pH = 11) was added to the colloidal phase. After the mixture was hand shaken for 5 min, it was centrifuged at 3000 rpm for 10 min. Finally, 20 μL of the aqueous extracting phase was withdrawn and injected into the HPLC system for analysis. The advantages of the proposed sample clean up are simplicity of operation, rapidity, high recovery, high enrichment factor, short extraction time and elimination of interference of a complex matrix. Since the extraction method used for this study reduced matrix effects, the relative recoveries of BPA were in the ranges of 98%–103.3%.

4. Conclusions

In this work, a fast and simple preparation method was developed and evaluated for the analysis of BPA in the water samples. The method offers several advantages such as simplicity, effectiveness and high enrichment factor. The replacement of organic extraction solvent with rhaminolipid biosurfactant lets Bio-DLLME achieve stable cloudy extraction media, rather than the original DLLME procedure. On the other hand, the consumption of toxic organic solvents in this method completely removed. Also, this study established a new and environmental friendly procedure for sample enrichment with methanol and rhaminolipid biosurfactant termed as Bio-DLLME. The extraction system can effectively accelerate the extractability in terms of the spontaneous formation of the micro emulsion structure as well as the enormous microinterfacial surface area.

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