



## ORIGINAL ARTICLE

# Determination of aromatic amines in environmental water samples by deep eutectic solvent-based dispersive liquid-liquid microextraction followed by HPLC-UV



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## KEYWORDS

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Bis(2-ethylhexyl) phosphate;  
Deep eutectic solvents;  
Environmental water samples;  
Microextraction

**Abstract** This study reports a deep eutectic solvent based dispersive liquid-liquid microextraction (DES-DLLME) to extract aromatic amines (4-chloroaniline, 3-nitroaniline, 2-naphtylamine) in environmental water samples before their HPLC-UV determination. The hydrophobic deep eutectic solvent (DES) was prepared by mixing bis(2-ethylhexyl) phosphate (BEHP) as a hydrogen bond acceptor and phenol as a hydrogen bond donor. Affecting factors on the extraction of the aromatic amines were investigated and optimized. Optimum conditions were: DES type: BHHP-Ph ratio: 1 to 2; pH of solution: 8.0; DES volume: 80  $\mu\text{L}$ , salt amount: 10% (w/v). Under optimum conditions, the developed method showed a wide linear range of 0.2–200  $\mu\text{g L}^{-1}$  ( $R^2 \geq 0.99$ ) with satisfactory recoveries ( $\geq 90.0\%$ ). The limit of detections (LODs) and limit of quantifications (LOQs) were in the range of 0.07–0.17  $\mu\text{g L}^{-1}$  and 0.2–0.5  $\mu\text{g L}^{-1}$ , respectively. The enrichment factors were 170, 180 and 190 for 4-chloroaniline, 3-nitroaniline, 2-naphtylamine, respectively. Based on obtained results, the proposed method is straightforward, efficient, sensitive, and eco-friendly for the extracting and determining of the aromatic amines in environmental water samples.

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## 1. Introduction

Aromatic amines (AAs) are important polar organic products and are widely used in many industrial fields such as pharmacy, manufacture of pesticides, and dyes (Katsumata et al., 2012). They can also be harmful products of diesel, rubber, combustion, etc. (Werner, 2020). Generally, this group of chemicals is considered hazardous to human health and involves inducing some types of cancers, including bladder

cancer (Dasgupta, 1998). Furthermore, the presence of AAs in the water resources can seriously be hazardous for aquatic creatures and human health. Therefore, the allowable contaminant level of AAs in water samples should be less than 30  $\mu\text{g/mL}$  (Werner, 2020). Therefore, it is vital to detect the content of AAs in water. Up to now, a variety of analytical methods, including gas chromatography (GC-FID) (Farajzadeh and Nouri, 2012; Han et al., 2013), gas chromatography-mass spectrophotometry (GC-MS) (Özkan et al., 2019; Zhang and Duan, 2019), high-performance liquid chromatography (HPLC-UV) (Werner, 2020; Wang et al., 2020), and liquid chromatography tandem mass spectrometry (LC-MS/MS) (Bie et al., 2017) have been applied to the analysis of AAs in aqueous matrices.

Due to the extremely low content of AAs in water samples and sometimes complexity of the studied matrices, a sample preparation method is required to enrich them and to reduce matrix effect.

Solid-phase extraction (SPE) (Hadjmohammadi et al., 2016), solid phase microextraction (SPME) (Zhang and Duan, 2019), dispersive liquid-liquid microextraction (DLLME) (Farajzadeh and Nouri, 2012; Zhou et al., 2010), deep eutectic solvent ultrasound assisted dispersive liquid-liquid microextraction (DES-UA-DLLME) (Werner, 2020), air-assisted liquid-liquid microextraction (AALLME) (Torbati et al., 2018), Dispersive micro-solid phase extraction (Jalilian et al., 2017), and monolith-based adsorbent/in-tip microextraction apparatus (MBA/ITMA) (Wang et al., 2020) are some of some pre-concentration methods adopting to AAs extraction from water samples.

Among the mentioned methods, the DLLME method is one of the most widely used micro-extraction methods in recent decades due to its simplicity, speed, low cost and high efficiency (Rezaee et al., 2010). One of the main trends in DLLME methods is to diversify the extraction solvents using solvents with features of multiple interactions, less toxicity, green and environmentally friendly. In this regard, DLLME techniques by using new generation green solvents including supramolecular solvents (SMSs), ferrofluid, ionic liquids (ILs), and deep eutectic solvents (DESs) are prevalent in the last decade due to their suitability for the rules of green analytical chemistry (ALothman et al., 2020; Zhu et al., 2021; Makoś et al., 2020; Li et al., 2020; Afshar Mogaddam et al., 2021; Elik et al., 2021; Yuvalia et al., 2021; Yelmaz and Soylak, 2018; Faraji et al., 2020a, Faraji et al., 2020b; Faraji, 2019a, Faraji, 2019b).

DESs have emerged as a superior substitute for the ILs with similar properties but their less toxicity and cost as well as their easy preparation. DES solvents can be easily synthesized by mixing a hydrogen bond acceptor (HBA) and one or two hydrogen bond donors (HBD) (Norae Nia and Hajmohammadi, 2021). The diversification of these solvents components and the possibility of creating various solvent interactions with target analytes have received considerable attention in recent years.

In this research, a novel DES was prepared by mixing bis(2-ethylhexyl) phosphate and phenol (BHEP-Ph) and used in DLLME method for pre-concentration of three aromatic amines (AAs) in water samples. The main factors affecting the current DES-DLLME procedure were investigated. Finally, the proposed method was coupled to HPLC-UV to analyze AAs in water samples and the satisfactory results proved the method's performance.

## 2. Materials and methods

### 2.1. Chemical and reagents

4-Chloroaniline (4-CA, purity  $\geq 99.0\%$ ), 3-nitroaniline (3-NA, purity  $\geq 98.0\%$ ), 2-naphtylamine (2-NA, purity  $\geq 99.0\%$ ), HPLC grade acetonitrile (ACN), bis(2-ethylhexyl) phosphate (BEHP, purity  $\geq 97.0\%$ ), octanoic acid (OA, purity  $\geq 99.0\%$ ), benzyltrimethylammonium chloride (BTEAC, purity  $\geq 97.0\%$ ), phenol (Ph, purity  $\geq 99.0\%$ ),

ammonium acetate (purity  $\geq 98.0\%$ ), and acetic acid (purity  $\geq 99.7\%$ ) were purchased from Sigma-Aldrich (Steinheim, Germany). The chemical structure of the studied AAs is shown in Fig. 1a. A stock solution of the PAAs at concentration level of 2000  $\text{mg L}^{-1}$  was prepared by dissolution of proper amounts of each AAs in methanol. The solution kept in the refrigerator and stable at least for 6 month. A mix working solution of AAs at a concentration level of 40  $\text{mg L}^{-1}$  was also prepared in methanol by suitable diluting.

### 2.2. Apparatus

Chromatographic separation was performed by EuroChrom model high-performance liquid chromatography (HPLC) from Knauer Germany. A Capital chromatography column with specifications of C8: 250  $\text{mm} \times 4.6 \text{ mm}$ , 5  $\mu\text{m}$  (Broxburn, UK) was used. The injection volume and detection wavelength was 20  $\mu\text{L}$  and 235  $\text{nm}$ , respectively. The elution of the analytes was done under isocratic elution by using a mobile phase of 0.1  $\text{mol L}^{-1}$  ammonium acetate buffer (pH = 7.0) and ACN (65:35, %v/v) at a flow rate of 1.0  $\text{mL min}^{-1}$ .

Fourier transform infrared (FTIR) spectra were measured with a PerkinElmer RXI spectrometer in the range of 400  $\text{cm}^{-1}$  to 4000  $\text{cm}^{-1}$  using the KBr method. Samples were centrifuged by an Universal 320R centrifuge from Hettich Zentrifugen (Tuttlingen, Germany). Samples were vortexed by a vortex-2 Genie vortex mixer from Scientific Industries (Bohemia, NY, USA).

### 2.3. Deep eutectic solvent preparation

Two hydrophobic DESs (BTEAC-octanoic acid and BEHP-phenol) were prepared by mixing 10 mmol of BTEAC and BEHP as the acceptor of hydrogen bonds (HBA) with 30 mmol of the octanoic acid and phenol as the donor of hydrogen bonds (HBD) in a round-bottom flask, respectively. The mixtures were stirred at 50  $^{\circ}\text{C}$  until the mixtures became clear and then the solvents kept at the ambient temperature.

### 2.4. Samples and analytical procedure

Three types of water samples were collected and analyzed. Lake water sample was collected from the Persian Gulf Martyrs Lake (Tehran, Iran). A fish pond water sample was collected from a fish farm from Karaj (Alborz, Iran). Tap water sample was collected from Standard Research Institute (Karaj, Iran). The samples were filtered by filter paper of 0.45  $\mu\text{m}$  and then kept in the refrigerator until before analysis. pH of the samples was adjusted and the extraction procedure was carried out.

For the microextraction of AAs from the samples via DES-DLLME method, 12.0 mL of sample was transferred to the falcon centrifuge tube. The optimization condition was conducted by adding 1.0 g sodium chloride (10%) to the sample and pH adjusted (pH = 6). Then, mixture of (80.0  $\mu\text{L}$  of DES (BHEP-Ph) + 100  $\mu\text{L}$  of methanol) was added to the solution as expeditiously as possible to disperse properly. The solution was vortexed vigorously for 1.0 min to get the complete dispersion of the solvent. the solution was centrifuged for 5.0 min (5000 rpm) to separate the extraction solvent from the aqueous phase. After centrifugation, two-phase



The results showed that BEHP-Ph composition shows better and higher efficiency in the extraction of AAs. The average recoveries for the AAs were 65% and 80% for BTEAC-OA and BEHP-Ph, respectively.

To acquire a better result, the effectiveness of various molar ratio has been considered; hence the combination of BEHP to phenol molar ratio (1:1, 1:2, 1:3, 1:4) was prepared and investigated. The obtained results (Fig. 2a) show that as the molar ratio increases, the extraction efficiency should increase slightly and become almost constant. Therefore, the 1:2 molar ratio of BEHP-Ph was chosen for subsequent studies.

### 3.2.2. Impact of pH

In this research, the pH was evaluated in the range of 2.0–9.5. According to Fig. 2b), the data display that enhancing pH

from 2 to 4.5 can cause substantial enhancement in the extraction efficiency and the maximum value achieved in the range of 4.5–7.0. After that, the extraction efficiency decreased by increasing pH. These changes in the diagram can be attributed by pKa values of compounds in the solution. As the pKa values of 4-CA, 3-NA, and 2-naphtylamine are 10.02, 11.58 and 9.84, respectively, we may conclude that reduction in the extraction efficiency at pH above 7.0 can cause by deprotonation of aromatic amines in the solution which is not favorable for ion-pairing mechanism. In addition, at alkaline pHs, the solubility of BEHP in the aqueous phase can be increased dramatically (Hansen et al., 2020). On the other hand, at pH = 2.0, BEHP is not in deprotonated form (pKa = 1.9) which is also not favorable for the ion-pairing mechanism. Eventually, to acquire an acceptable result acetic acid/acetate

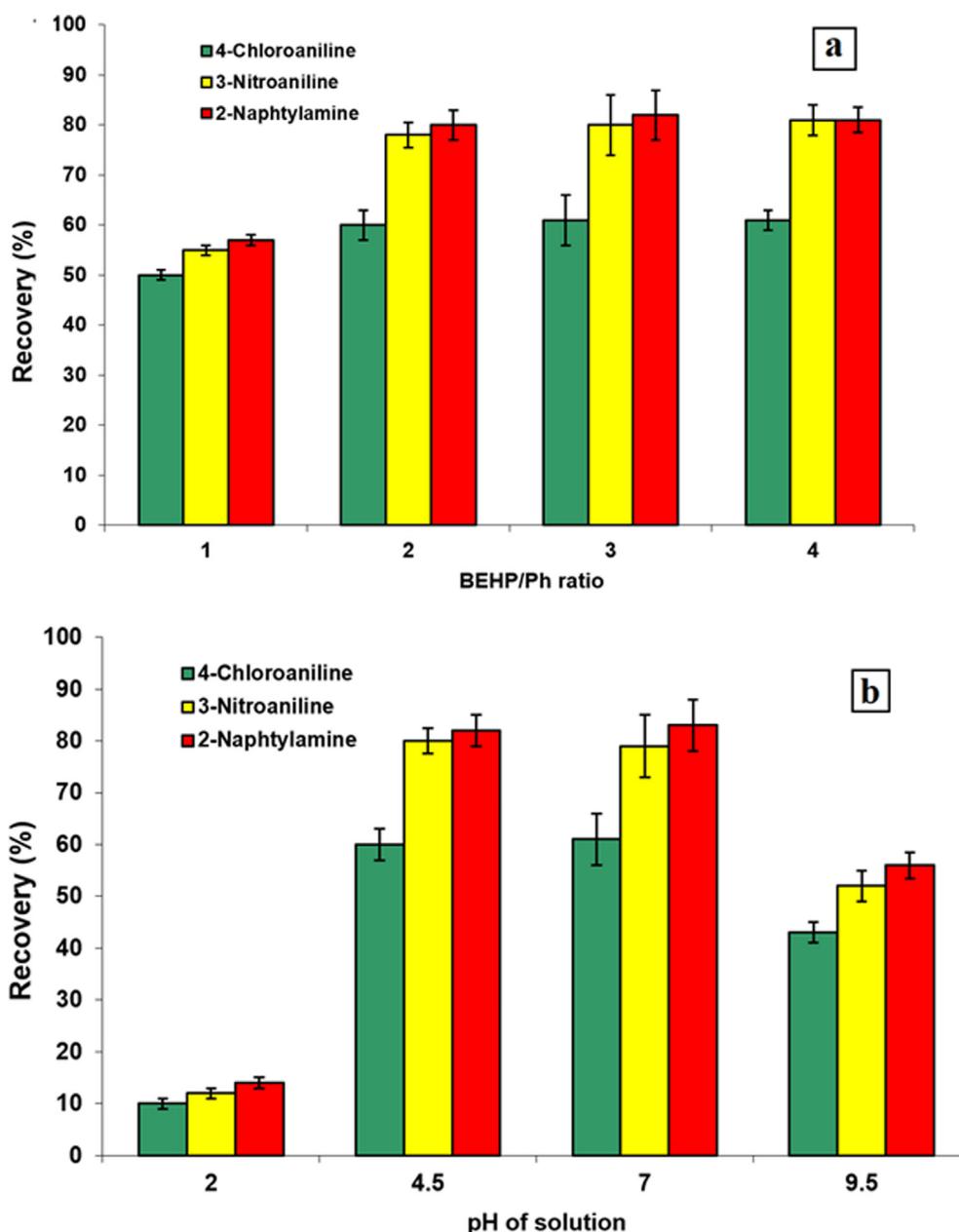


Fig. 2 Effect of pH on the extraction of the PAAs (a), Effect of DES composition on extraction of PAAs (b).

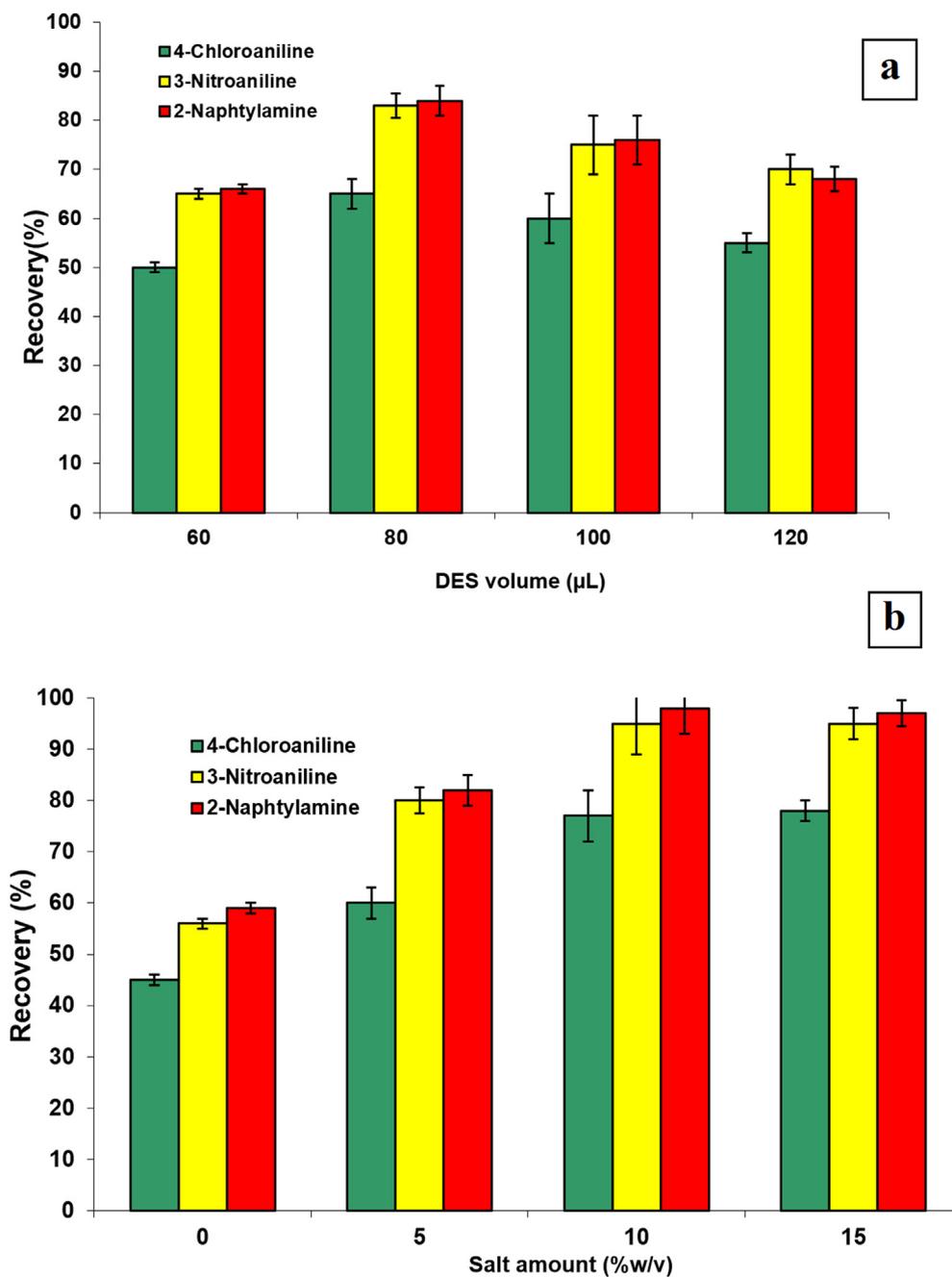
buffer ( $10 \text{ mmol L}^{-1}$ ) at  $\text{pH} = 4.5$  was chosen as the optimum condition for the extraction.

### 3.2.3. Influence of DES volume

The effect of different volumes of the DES ( $60 \mu\text{L}$ ,  $80 \mu\text{L}$ ,  $100 \mu\text{L}$ ,  $120 \mu\text{L}$ ) was investigated. By enhancing DES volume from  $60$  to  $80 \mu\text{L}$ , extraction efficiency rose. However, further increases in the volume of the DES lead to decreasing signal as a result of the dilution effect (Faraji, 2019a, Faraji, 2019b). Therefore, based on Fig. 3a,  $80 \mu\text{L}$  was selected as an optimum DES volume for subsequent studies.

### 3.2.4. Influence of salt concentration

As the salt concentration increases, the extraction efficiency usually increases due to the salting-out phenomenon, this increasing effect can be offset by increasing the volume of the extraction phase. For this reason, the influence of the different amounts of sodium chloride was evaluated in the range of  $0.0$ – $15.0\%$  (w/v). According to Fig. 3b, by increasing salt amount, the extraction recoveries of the AAs increase and then remains almost constant. Therefore,  $10.0\%$  NaCl was chosen for further studies.



**Fig. 3** Effect of DES volume on extraction efficiency of aromatic amines (a), Effect of salt concentration on extraction of aromatic amines (b).

**Table 1** Analytical features of the proposed method.

Analyte	RSD				LOD( $\mu\text{g L}^{-1}$ )	LOQ( $\mu\text{g L}^{-1}$ )	EF
	Inter-days (n = 6)		Intra-day (n = 3)				
	5.0( $\mu\text{g L}^{-1}$ )	25( $\mu\text{g L}^{-1}$ )	5.0( $\mu\text{g L}^{-1}$ )	25( $\mu\text{g L}^{-1}$ )			
4-Chloroaniline	5.8	4.7	1.9	2.1	0.17	0.5	170
3-Nitroaniline	3.8	3.2	3.5	2.2	0.1	0.3	180
2-Naphtylamine	3.7	3.8	2.1	1.8	0.07	0.2	190

RSD: Relative standard deviation; LOQ: Limit of quantification; LOD: Limit of detection; EF: Enrichment factor.

### 3.2.5. Effect of vortex time

An effective solution vortex can accelerate the transfer of the analyte from the aqueous solution to the DES phase. Therefore, the effect of vortex time was investigated in the range of 1.0–3.0 min. According to obtained results; extraction efficiency was almost constant in the studied range. Therefore, 1.0 min vortex was chosen for further studies.

### 3.3. Analytical performance

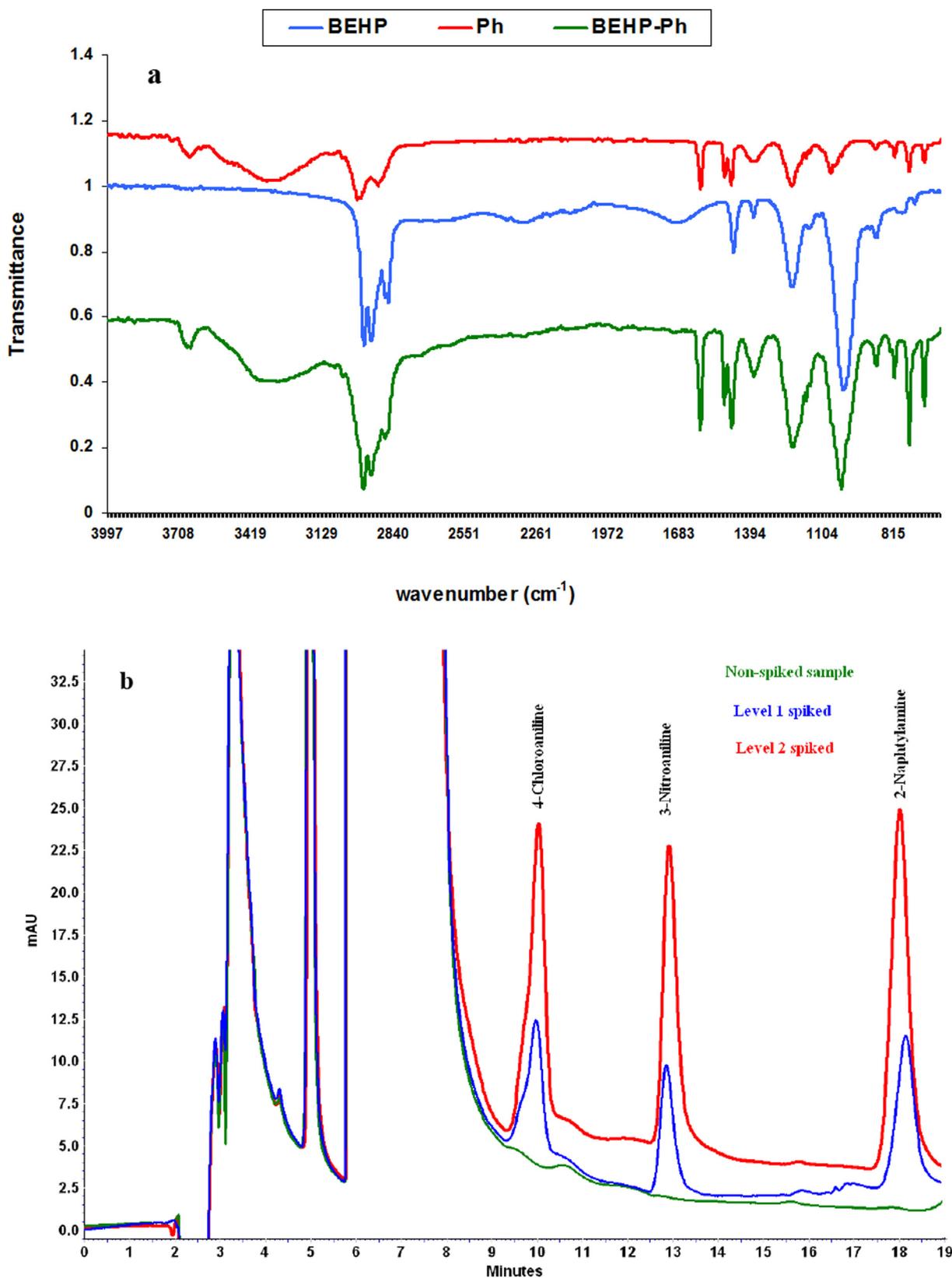
Under optimal conditions, the performance of the developed method was evaluated by considering linear dynamic range (LDR), precision (intra-day and inter-day), the limit of detection (LOD), the limit of quantification (LOQ), and enrichment

factor (EF). The figures of merit of the developed technique are presented in Table 1. The calibration curve was linear in the range of 0.5–200  $\mu\text{g L}^{-1}$ , 0.3–200  $\mu\text{g L}^{-1}$ , and 0.2–200  $\mu\text{g L}^{-1}$ , for 4-CA, 3-NA, and 2-naphtyl amine, respectively ( $R^2 \geq 0.99$ ). Intra-day and inter-day RSD values are less than 6.0% at concentration levels of 5.0 and 25  $\mu\text{g L}^{-1}$ . The LOD values based on  $S/N = 3$  were 0.17, 0.1 and 0.07  $\mu\text{g L}^{-1}$  for 4-CA, 3-NA, 2-naphtylamine, respectively. Also, the LOQ values based on  $S/N = 10$  were 0.5, 0.3 and 0.2  $\mu\text{g L}^{-1}$  for 4-CA, 3-NA, 2-naphtylamine, respectively. The enrichment factors (EFs) were calculated as the ratio between analyte concentrations in the acceptor phase (DES phase) to the initial concentration in the sample. EFs were 170, 180 and 190 for 4-CA, 3-NA, and 2-naphtyl amine, respectively.

**Table 2** Analysis of aromatic amines in water samples by applying the developed method.

Sample	Analyte	Added ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Relative recovery (%)	RSD% (n = 3)
Tap water	4-Chloroaniline	–	N.D	–	5.7
		10.0	9.2	92.0	4.2
		20.0	19.4	97.0	3.8
	3-Nitroaniline	–	N.D	–	4.1
		5.0	4.7	94.0	3.9
		10.0	9.8	98.0	2.5
	2-Naphtylamine	–	N.D	–	4.5
		5.0	4.9	98.0	4.1
		10.0	9.7	97.0	3.7
Lake water	4-Chloroaniline	–	N.D	–	3.4
		10.0	9.2	92.0	4.7
		20.0	19.7	98.5	5.4
	3-Nitroaniline	–	N.D	–	2.6
		5.0	4.5	90.0	4.9
		10.0	9.5	95.0	3.8
	2-Naphtylamine	–	N.D	–	4.3
		5.0	4.8	96.0	5.3
		10.0	9.4	94.0	4.7
River water	4-Chloroaniline	–	N.D	–	2.9
		10.0	9.3	93.0	5.3
		20.0	19.2	96.0	4.7
	3-Nitroaniline	–	N.D	–	2.5
		5.0	4.6	92.0	4.3
		10.0	9.3	93.0	2.8
	2-Naphtylamine	–	N.D	–	4.4
		5.0	4.8	96.0	5.1
		10.0	9.9	99.0	2.8

N.D: not detected.



**Fig. 4** FT-IR spectrum of BEHP (blue), Ph (red) and BEHP-Ph (green) (a). Chromatograms of lake water before and after spike of level 1 (10, 5.0 and 5.0  $\mu\text{g L}^{-1}$  respect to 4-CA, 3-NA, 2-naphthylamine, respectively) and level 2 (20, 10.0 and 10.0  $\mu\text{g L}^{-1}$  respect to 4-CA, 3-NA, 2-naphthylamine, respectively) of the standard solutions of PAAs (b).

**Table 3** Comparison of the developed technique with some recently published techniques in analysis of the AAs.

Analyte	Sample preparation	Instrumentation	Solvent/adsorbent	LR <sup>a</sup> (µg/L)	LOD <sup>b</sup> (µg/L)	RSD <sup>c</sup> (%)	EF <sup>d</sup>	Ref.
Aniline, <i>p</i> -methylaniline, 2,4-dinitroaniline, 2-nitroaniline, 2-chloroaniline, diphenylamine, 3,4-dichloroaniline	MBA/ITMA <sup>c</sup>	HPLC-UV <sup>f</sup>	Monolith-based adsorbent	0.01–300	0.0021–0.026	0.85–11	2.7–8.1	Wang et al., 2020
4 Aminobiphenyl, 4 Chloro 2 methylaniline, Benzidine, 2 Naphthylamine, 4 Chloroaniline, 3,3' Dimethylbenzidine, <i>p</i> Cresidine, 4 Aminoazobenzene	DLLME <sup>h</sup>	GC-MS <sup>i</sup>	chloroform and 1,2 dichloroethane	0.5–250	0.16–1.4	less than 10	43–231	Özkan et al., 2019
3-Nitroaniline 4- chloroaniline 4- bromoaniline 3,4- dichloroaniline	D-µ-SPE <sup>j</sup>	HPLC-UV	Multi-walled carbon nanotubes/ Fe3O4@Poly(1,8-diaminonaphtalen)	0.25–500	0.1–0.25	3.4–5.6	40–65.7	Jalilian et al., 2017
Aniline, <i>o</i> -toluidine, 2-Chloroaniline, <i>o</i> -Anisidine, 4-Chloroaniline	DLLME	GC-FID <sup>k</sup>	Butylchloroformate	10–10000	1–3	less than 5.2	197–298	Farajzadeh and Nouri, 2012
Aniline, N,N-dimethylaniline, <i>o</i> -toluidine, <i>m</i> -toluidine and <i>p</i> -toluidine.	DLLME	GC-FID	Chlorobenzene	4–1000	0.2–3.4	1.2–7.9	207–4315	Han et al., 2013
<i>o</i> -nitroaniline, alpha-naphthylamine, <i>o</i> -chloroaniline	DLLME	HPLC-UV	Chlorobenzene	1–50	0.1–0.7	6.3–9.7	N/R	Zhou et al., 2010
4-nitroaniline, para toluidine, 4-chloroaniline, 2-nitroaniline, 3-nitroaniline, 3-chloroaniline, 4-bromoaniline	SPE	MLC <sup>l</sup>	C18 cartridge	3.1–125.0	1–4.5	5.8	N/R	Hadjmohammadi et al., 2016
Aniline, N-methylaniline, 2-methylaniline, 2,6-dimethylaniline, 2-methoxyaniline, 2-chloroaniline, 4-chloroaniline, 1-naphthylamine, 2-chloroaniline, 4-chloroaniline	SPME <sup>m</sup>	GC-MS	Polymeric ionic liquid fiber	10–10,000	0.67–4.29	2.1–8.3	N/R	Zhang and Duan, 2019
2-chloroaniline, 4-chloroaniline	DES-UA <sup>n</sup> -DLLME-SAP <sup>o</sup>	HPLC-UV	Trihexyl phosphonium chloride and decanol	N/Rg	0.07–0.11	2.9–6.2	116–121	Werner, 2020
Aniline, <i>p</i> -toluidine, <i>p</i> -chloroaniline, <i>p</i> -anisidine, 4- <i>tert</i> -butyl aniline	AALLME <sup>p</sup>	GC-MS	Choline Chloride <i>n</i> -butyric acid	N/R	1.8–6	≤5.3	790–940	Torbati et al., 2018
<i>o</i> -toluidine ( <i>o</i> -TOL), 2, 6-dimethylaniline (2, 6-DMA), <i>o</i> -anisidine ( <i>o</i> -ASD), 1-naphthylamine (1-ANP), 2-naphthylamine (2-ANP), and 4-aminobiphenyl (4-AB)	SPE	LC-MS/MS <sup>q</sup>	C18 cartridge	0.1–50	0.04–0.58	4.13–8.42	N/R	Bie et al., 2017
4-Chloroaniline, 3-Nitroaniline, 2-naphthylamine	DES-DLLME	HPLC-UV	Bis(2-ethylhexyl) phosphate- phenol	0.2–200	0.07–0.17	1.8–5.8	170–190	This work

<sup>a</sup>: Linear range, <sup>b</sup>: Limit of detection, <sup>c</sup>: Relative standard deviation, <sup>d</sup>: Enrichment factor, <sup>e</sup>: In-tip microextraction apparatus monolith-based adsorbent, <sup>f</sup>: High performance liquid chromatography-Ultra violet detection <sup>g</sup>: Not reported, <sup>h</sup>: Dispersive liquid-liquid microextraction, <sup>i</sup>: Gas chromatography-mass spectrometry, <sup>j</sup>: Dispersive micro-solid phase extraction, <sup>k</sup>: Gas chromatography-flame ionization detector <sup>l</sup>: Micellar liquid chromatography, <sup>m</sup>: Solid phase microextraction, <sup>n</sup>: Ultrasound-assisted, <sup>o</sup>: Solidification of the aqueous phase, <sup>p</sup>: Air-assisted liquid-liquid microextraction, <sup>q</sup>: Liquid chromatography coupled with tandem mass spectrometry.

### 3.4. Real sample analysis

The applicability of the developed method in real sample analysis was evaluated by analyzing some water samples under optimum conditions. The data are presented in Table 2. The concentration of the studied AAs in the water sample was

below the LOD. Therefore, to verify the accuracy of the method, the samples were spiked at known concentration levels of PAAs. Good relative recoveries ranged from 90.0 to 98.0 with RSD less than 7.0% were obtained by analyzing three independent samples. Chromatogram of the lake water sample before and after the spike of level 1 (10, 5.0 and

5.0  $\mu\text{g L}^{-1}$  respect to 4-CA, 3-NA, 2-naphtylamine, respectively) and level 2 (20, 10.0 and 10.0  $\mu\text{g L}^{-1}$  respect to 4-CA, 3-NA, 2-naphtylamine, respectively) of mixture standard solution of the PAAs is shown in Fig. 4.

### 3.5. Comparison of proposed technique with previously published techniques

The proposed method was compared with some of the methods that recently reported in the literatures for the extraction and determination of AAs in aqueous matrices (Table 3). As it can be seen, the linearity, detection limit, repeatability and enrichment factor of the proposed method are better or comparable to the LC-MS (Bie et al., 2017) and GC-MS (Ozkan et al., 2019; Torbati et al., 2018; Zhang and Duan, 2019) methods. In particular, the cost, time, simplicity, and repeatability of the proposed method are better and more appropriate than the SPE (Jalilian et al., 2017). The extraction solvent used in our proposed method, same as other DES based methods (Torbati et al., 2018; Werner, 2020), is safer than classical solvent based DLLME methods (Ozkan et al., 2019; Farajzadeh and Nouri, 2012, Han et al., 2013; Zou et al., 2010). However, extraction solvent separation in DES based methods is a bit difficult and usually an additional centrifugation step is required to complete separation of DES phase because of higher viscosity of DES solvents compared to the classical solvents that can stick to the walls of the vials. It should be noted that the analysis of AAs by GC-FID (Farajzadeh and Nouri, 2012, Han et al., 2013; Zou et al., 2010) or GC-MS (Ozkan et al., 2019; Torbati et al., 2018) compared to LC-based methods (Wang et al., 2020, Jalilian et al., 2017, Werner, 2020, Bie et al., 2017), requires a polar column or a derivatization step which complicates the method and reduces its greenness. However, GC-based methods offer higher enrichment factors than LC-based methods due to the greater compatibility of DLLME with GC techniques (Rezaee et al., 2010). Accessibility, simplicity and cost of reagents and instrument, the proposed methods are better than MS-based methods, but sensitivity, reliability and selectivity of MS-based methods are better than the proposed method.

## 4. Conclusion

In this study, a new hydrophobic DES solvent is developed to extract AAs from aqueous samples. The DES was prepared by mixing BEHP as HBA and phenol as HBD. According to the nature of the DES components, strong ion-pairing and  $\pi$ - $\pi$  interactions could occur between target analytes and the solvent leading to superior extraction efficiencies (satisfactory recoveries within the range of 81.0–94.7% and high precision (RSD less than 6.7%)). Overall, the developed method presents an environmentally friendly and sensitive method for the extraction and enrichment of trace amounts of 4-CA, 3-NA, 2-naphtylamine in water samples. Meanwhile, the proposed method has great potential application value in water or other samples monitoring of PAAs.

## Availability of data and material

The data which support the findings of this research are available from the corresponding author.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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