



Anal. Bioanal. Chem. Res., Vol. 8, No. 2, 163-176, April 2021.

Application of Magnetic Metal Organic Framework for Dispersive Solid Phase Extraction of Bisphenol A from Water

E. Karimnia^a, E. Ghorbani-Kalhor^{a,*}, K. Farhadi^b, M.T. Vardini^a and R. Molaei^c

^a*Department of Chemistry, Tabriz Branch, Islamic Azad University, Tabriz, Iran*

^b*Department of Analytical Chemistry, Faculty of Chemistry, Urmia University, Urmia, Iran*

^c*Department of Food Hygiene and Quality Control, Faculty of Veterinary Medicine, Urmia University, Urmia, Iran*

(Received 17 June 2020 Accepted 31 October 2020)

An efficient method was developed for the synthesis of amino functionalized magnetic metal organic framework composite ($\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$) and the prepared composite was used as an adsorbent in magnetic solid-phase extraction (MSPE) for the separation and enrichment of Bisphenol A (BPA) from water samples followed by high performance liquid chromatography analysis. The prepared framework composite was characterized using transmission electron microscopy, x-ray diffraction, Fourier-transform infrared spectroscopy, Brunauer-Emmett-Teller and vibrating sample magnetometer techniques. Several parameters affecting the efficiency of magnetic separation including the amount of adsorbent, extraction time, desorption solvent, and desorption volume were optimized. Under optimum conditions, the response of the method was linear over the concentration range of 0.1-20 ng ml^{-1} for studied BPA. The limit of detection of the method was 0.03 ng ml^{-1} at a signal-to-noise ratio of 3 with an RSD of lower than 6.5%. Finally, the proposed method was successfully applied for the determination of trace amounts of target analyte in mineral water samples.

Keywords: Magnetic solid phase extraction, Magnetic metal-organic framework, Bisphenol A, Water samples

INTRODUCTION

Bisphenol A (4,4'-dihydroxy-2,2-diphenylpropane, commonly named BPA) was first synthesized in 1905. BPA is currently used as a monomer in the preparation of polycarbonate (a hard and clear polymer) plastics and epoxy resins and as an additive in polyvinyl chloride [1]. Due to the hardness, transparency, durability and heat stability of these polymers, they are commonly used in the fabrication of plastic bottles and storage containers (polycarbonate plastic) and are applied as a lacquer to coat metal products such as bottles tops, water pipes, food cans, and dental composites (epoxy resins). The annual production of several million tons of BPA for manufacturing polycarbonate plastic has made it one of the most commonly used chemicals in the world [2]. From safety standpoint, BPA

can transfer these plastics and easily enter human body to create adverse health effects such as increased risk of liver enzyme abnormalities, cardiovascular diseases and diabetes mellitus [3]. BPA levels detected in water samples collected from these containers ranged from 2.4-14.3 $\mu\text{g l}^{-1}$ and up to 228-521 $\mu\text{g l}^{-1}$ after heating at 70 °C for six days [4]. The reference established by US Environmental Protection Agency is 50 $\mu\text{g BPA kg}^{-1}$ body weight/day [5]. In response to these challenges, regulating corporations have taken proceedings to restrict the use of BP in food packaging products [6].

To date, various analytical methods have been developed and utilized for the quantitation of BPA. These methods include gas chromatography-mass spectrometry (GC-MS), liquid chromatography (LC), liquid chromatography with electrochemical detector (LC-ECD), liquid chromatography-mass spectrometry (LC-MS), enzyme-linked immunosorbent assay (ELISA),

*Corresponding author. E-mail: ekalhor@iaut.ac.ir

Table 1. Previously Reported Analytical Methods for the Determination and Quantification of BPA in Various Matrices; Comparison with the Proposed Method

Matrix	Analytical technique /detector	Sample preparation method ^a	LOD (ng ml ⁻¹)	LOQ (ng ml ⁻¹)	Ref.
Sea waters	HPLC-UV	SDME	4	9	[42]
Sea waters	HPLC-UV	DLLME	0.2	1.6	[42]
Landfill leachate	HPLC-UV	DLLME	1.5	-	[19]
River water, body fluid	GC-MS	SBSE	0.005	0.02	[15]
Canned food	GC-MS	SPME	0.1	0.3	[43]
River water	GC-MS	LPME	0.002	0.01	[17]
Water	HPLC-DAD	MIP-SPME	250	700	[44]
Body fluid	LC-MS	SPE	-	0.01	[45]
River water	HPLC-FL	M-MIPs	0.05	0.1	[46]
Mineral water	HPLC-DAD	M-MOF	0.03	0.1	This work

^aSDME; Single-drop microextraction, DLLME: Dispersive liquid liquid microextraction, SBSE: Stir bar sorptive extraction, SPME: solid-phase microextraction, LPME: Liquid-phase microextraction, MIP: Molecularly imprinted polymer.

chemiluminescence and electrochemical techniques [7-12].

However, the main issues in assessment of BPA level are the complication of sample matrices and their low concentrations, indicating that proper sample preparation methods are essential for improving determination selectivity and sensitivity. Unlike classic sample preparation methods that consume relatively large amounts of organic solvents, microextraction methods have been illustrated to increase analyte enrichment and reduce the use of organic solvents and chemicals [13].

In literature, some sample preconcentration procedures such as single-drop liquid-phase microextraction (SDME) [14], stir bar sorptive extraction (SBSE) [15], solid-phase microextraction (SPME) [16], liquid-phase microextraction (LPME) [17], molecularly imprinted solid-phase extraction (MISPE) [18] and dispersive liquid-liquid microextraction (DLLME) [19] have been introduced for the pretreatment of BPA-containing samples. Table 1 represents the limit of detection, limit of quantitation and employed sample

preparation procedures in some previously reported analytical techniques and proposed method for the determination of BPA in some biological, environmental and food samples.

Metal-organic frameworks (MOFs) are a novel and innovative class of hybrid porous coordination polymers with vast uniform framework structures [20].

Chemical and electrochemical methods are the two primary methods of constructing MOFs. In chemical methods, MOFs are usually made by collaborative ionic interaction between metal salts and organic linkers in a mixed solution [21]. Due to the simplicity of the process and possibility of fabricating large-scale MOFs, chemical procedures are often preferred, especially when analytical applications (such as sensing, separation, *etc.*) are considered.

MOFs are promising in separation applications due to their notable flairs such as diverse structure types and compositions, tunable pore size, and surface areas ranging

from 200-7000 m² g⁻¹ [22], that allow MOFs to be desirable sorbents for extraction [23]. Also, they have well-modified surface characters, permitting easy access to functional groups [24]. Besides, lipophilic properties and π - π interactions provide MOFs with stronger affinity to aromatic pollutants than common sorbents during sample pretreatments [21]. Accordingly, MOFs can be applied to extract various types of analytes, such as lipophilic compounds, polar compounds, and metal ions, in various sample matrices including water, food and biological samples [25,26].

The application of MOFs as sorbents for SPME was first reported by Cui *et al.* [27] and their results showed that MOFs were favorable for rapid, efficient, and convenient SPME of different aromatic compounds from environmental water samples [28,29]. In a recent work from Yamini and Safari, the as-prepared magnetic framework composites (Fe₃O₄@TMU-21) were used as the efficient adsorbents for the extraction of trace pyrethroid residues in samples obtained from fruit juice [30]. Also, Salimi *et al.* developed a method for the trace monitoring of some nitrophenols in various environmental water samples based on zirconium-based amino-tagged MOFs as nanosorbents [31]. Herein, a dispersive solid phase microextraction method based on magnetic metal organic framework (Fe₃O₄-NH₂@MOF-235) is established as a novel adsorbent for the separation and preconcentration of BPA before sensitive determination by HPLC with UV detection (HPLC-UV). The experimental parameters influencing the preconcentration of BPA by presented method were optimized. The proposed method was applied for the determination of trace amounts of BPA in mineral water samples with satisfactory results.

MATERIALS AND METHODS

Materials and Reagents

All reagents and standards were at least of analytical grade. Bisphenol A (BPA) standard as a model analyte was supplied by Sigma-Aldrich (USA). Ferric chloride hexahydrate (FeCl₃·6H₂O), ethylene glycol (C₂H₆O₂), 1,6-hexanediamine (C₆H₁₆N₂), terephthalic acid (H₂BDC), sodium acetate (C₂H₃NaO₂), hydrochloric acid and sodium hydroxide were purchased from Merck (Darmstadt,

Germany). Acetone, acetonitrile, 1-dodecanol (C₁₂H₂₆O), methanol and ethyl acetate were also provided by Merck (Darmstadt, Germany). HPLC-grade water and methanol (MeOH) were supplied from Daejung-Chemical and Metals Co. Ltd. (Kyeonggi-Do, South Korea). Deionized water (DI) was obtained from Atlas Shimi Company (Tehran, Iran) and was used wherever needed. All solvents and buffers were filtered and sonicated before use.

Apparatus and Chromatographic Conditions

The particle sizes and surface morphologies of the prepared adsorbent were studied using transmission electron microscopy (TEM, JEM-200CX, JEOL, Japan). X-ray diffraction (XRD) patterns of the synthesized composites were obtained using an X-ray powder diffractometer (Philips PW-1730, Japan). Fourier-transform infrared (FT-IR) spectra were recorded on an FT-IR-Nicolet iS20 spectrometer (Thermo Fischer Scientific). The magnetic characteristics of all products were investigated using a vibrating sample magnetometer (VSM, Lake Shore 7410, USA).

A Knauer HPLC (Berlin, Germany) consisting of a smart line 1000 solvent pump unit, a vacuum degasser, a Rheodyne 7725 injector of 20 μ l loop volume (USA) and a K-2600 UV detector (Knauer, 152 Germany) were used for the determination of BPA. Separation was performed on a reverse phase C₁₈ HPLC column (5 μ m, 150 \times 4.6 mm i.d.) (Knauer, Germany) using the mixture of methanol and water (60:40, v/v) as a mobile phase at a flow rate of 0.8 ml min⁻¹. Temperature was set to 30 °C. Detection wavelength was 278 nm for the studied analyte.

Preparation of Amine-functionalized Fe₃O₄ Particles (Fe₃O₄-NH₂)

Fe₃O₄-NH₂ particles was prepared using the method explained previously by Wang *et al.* [32], with some modifications. Briefly, in a typical synthesis of Fe₃O₄-NH₂ particles, FeCl₃·6H₂O (1.0 g) and sodium citrate (2.0 g) were dissolved in 30 ml ethylene glycol forming homogeneous solution, 1,6-hexanediamine (5 ml) was added into mixture solution and vigorous stirring was continued for 30 min at 50 °C. Then, the resulting mixture was transferred to a 50 ml Teflon-lined stainless-steel autoclave and heated at 180 °C for 7 h. Eventually, the

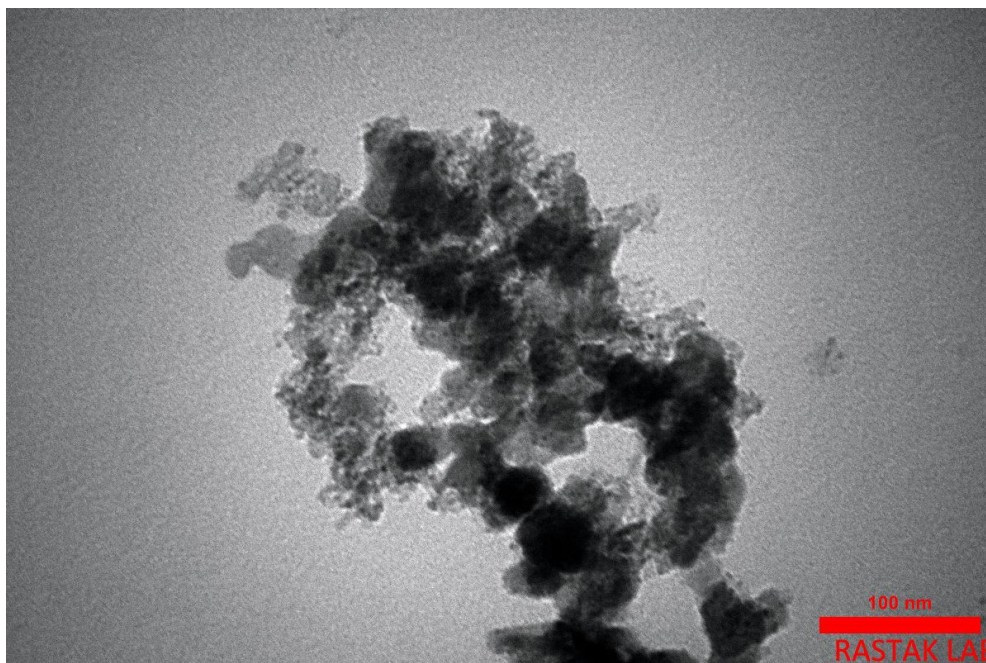


Fig. 1. TEM image of the prepared magnetic composite $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$.

mixture was rinsed with ethanol several times. Afterward, the black product was desiccated under vacuum for 12 h at 70 °C.

Synthesis of $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$

Typically, $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (100 mg, 0.369 mmol) and H_2BDC (102.5 mg, 0.615 mmol) were dissolved in 30 ml DMF by magnetic stirring for 30 min. In the next step, the pre-synthesized $\text{Fe}_3\text{O}_4\text{-NH}_2$ particles (100 mg) were dispersed into 5 ml DMF under ultra-sonication for 30 min and then the above mixture was poured while stirring. The resulting suspension was transferred to a Teflon-lined stainless-steel autoclave and heated at 80 °C for 24 h. The obtained product was gathered by a magnet followed by washing with DMF and ethanol for several times. Finally, the product was dried under vacuum for 12 h at 70 °C.

MOF-MSPE Procedure

At first, 150 mg $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ composite was poured into a glass test tube containing 25 ml sample solution (containing 1.0 ng ml^{-1} of BPA) and was homogeneously mixed. The mixture was then put in a

vortex mixer for 5 min to improve the sorption of the studied analyte onto the as-prepared adsorbent. Subsequently, the magnetic sorbent was collected from the matrix solution using an external magnetic field and the supernatant was discarded. For the desorption of the retained BPA, 200 μl ethyl acetate was added to analyte-loaded sorbent and sonicated for 1 min. The sorbent was held by the application of an external magnet. The ethyl acetate phase was transferred into a test tube and dried with a mild nitrogen stream. Finally, the residue was dissolved in 0.5 ml mobile phase solvent using sonication for 30 s. Finally, 10 μl of the final solvent was injected into HPLC device for further analysis. The sorbent was regenerated through further rising with ethyl acetate solution and water several times.

RESULTS AND DISCUSSION

Characterization of the $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ Composite

The shape and size of MOF magnetic nanocomposite were characterized by TEM (Fig. 1). The captured

micrographs of the as-prepared magnetic nanocomposite revealed a highly porous structure with dimensions within nanometer range, such that this porous structure meliorated the potency of MOF to adsorb the studied BPA. The size of synthesized $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ composite was much smaller than those reported in literature [33]. However, this value was lower than those of MOF prepared by ultrasonic

method due to nonporous Fe_3O_4 cavities in hollow magnetic materials. The specific surface area of porous $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ was far higher than most of other magnetic porous materials.

The structural information of $\text{Fe}_3\text{O}_4\text{-NH}_2$ and $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ magnetic samples were analyzed by XRD. As shown in Fig. 2A, $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$

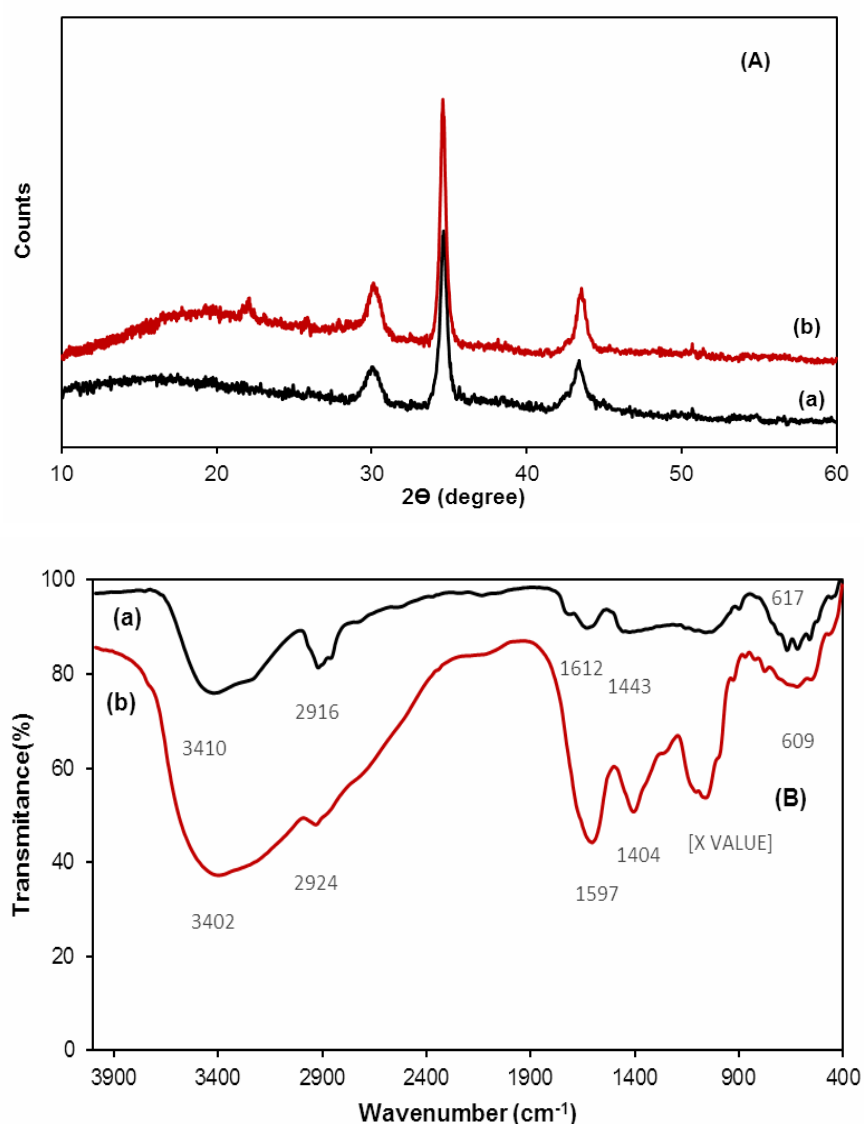
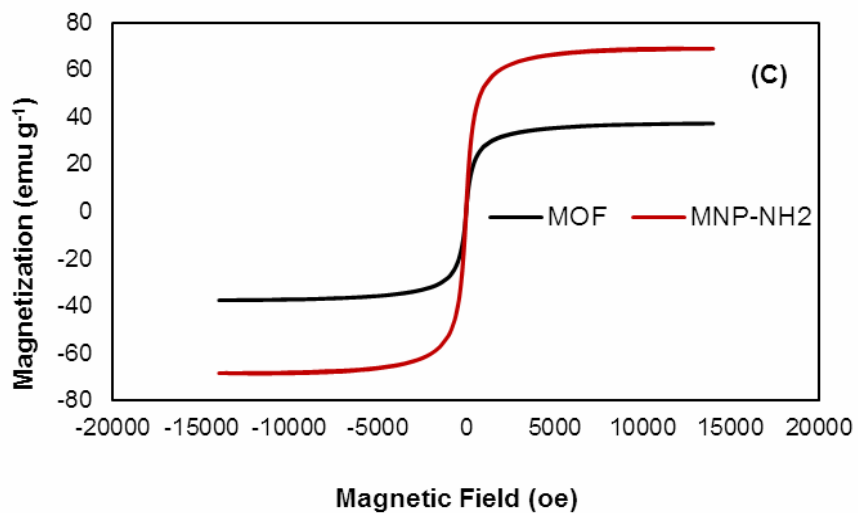


Fig. 2. (A) XRD spectra of the prepared $\text{Fe}_3\text{O}_4\text{-NH}_2$ (a) and $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ (b), (B) FTIR spectra of $\text{Fe}_3\text{O}_4\text{-NH}_2$ (a) and $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ (b), (C) The magnetization curves of $\text{Fe}_3\text{O}_4\text{-NH}_2$ particles and the $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ composite, (D) BET plot (left) and N_2 sorption-desorption isotherms (right) of the as prepared $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ composite.



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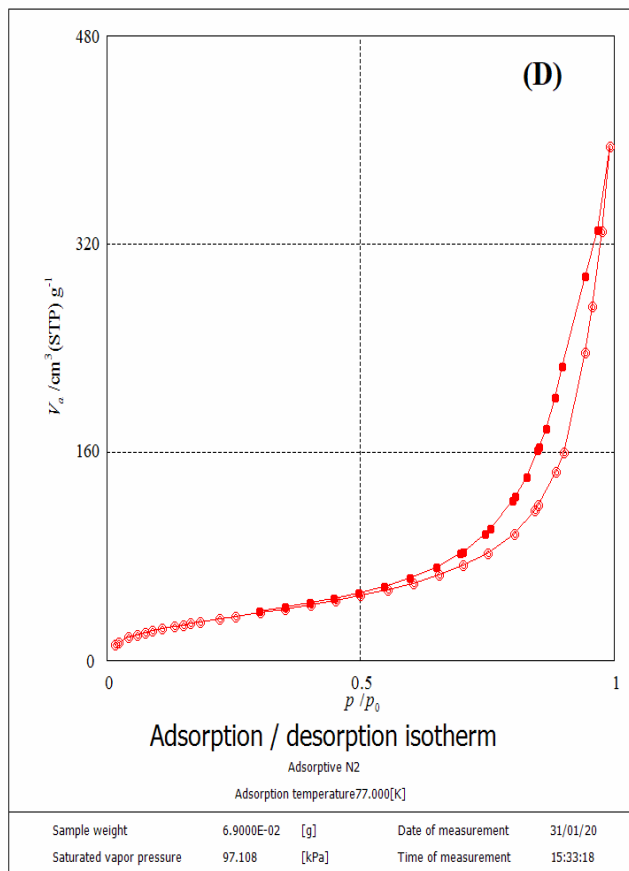
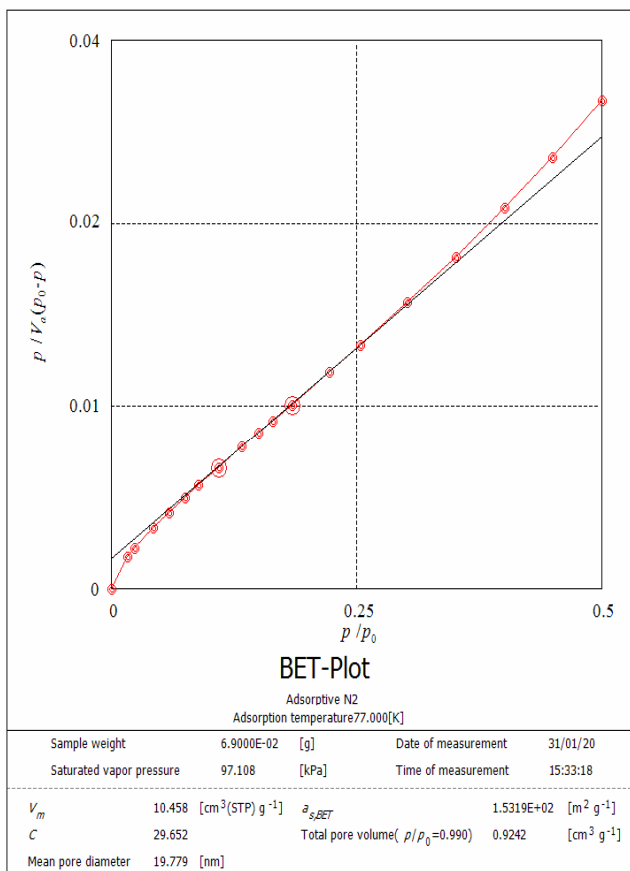


Fig. 2. Continued.

composite presented characteristic diffraction peaks at $2\theta = 18^\circ, 22^\circ$ and 33° , which were in good consistency with previously reported literature for hexagonal single crystals of MOF-235 [34], and magnetic $\text{Fe}_3\text{O}_4\text{-NH}_2$ particles ($2\theta = 30^\circ, 35^\circ$ and 43°) displayed the coexistence of MOF-235 particles and magnetic $\text{Fe}_3\text{O}_4\text{-NH}_2$ materials. Moreover, it displayed the representative peaks of iron oxide nanoparticles, which confirmed the right modification of MOF-235 [35,36]. The successful synthesis of iron(III)-based framework composites was confirmed by the XRD patterns and that the insertion of magnetic particles to MOF crystals did not destroy the crystal structure of frameworks.

In Fig. 2B, the FT-IR spectra of $\text{Fe}_3\text{O}_4\text{-NH}_2$ particles (a) and $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ (b) are shown. A sharp band at 609 cm^{-1} , observable in the spectra of all magnetic materials, could be ascribed to the stretching vibrations of Fe-O bond, which was considered as the evidence for the successful modification of Fe_3O_4 nanoparticles with desired MOF [36]. Also, the broad absorption bands centered around 3400 cm^{-1} in both spectra could be associated with stretching vibrations of -OH and -NH groups and spectral bands located at 2916 (Fig. 2B-a) and 2924 (Fig. 2B-b) could be assigned to the vibrational mode of C-H [36]. Likewise, several characteristic peaks related to C=O and C=C in H_2BTC appeared at 1597 and 1404 cm^{-1} , respectively, which indicated the successful garniture of MOF-235 on the surface of $\text{Fe}_3\text{O}_4\text{-NH}_2$.

The magnetic behavior of the as-prepared composites was appraised using vibrating sample magnetometry (VSM) at 300 K. As shown in Fig. 2C, the saturation magnetization values of $\text{Fe}_3\text{O}_4\text{-NH}_2$ and $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ were 69.21 and 37.13 emu g^{-1} , respectively, and their durability and coercivity values were zero. According to coercivity values and determined size, it could be concluded that the synthesized nanocomposites had superparamagnetic properties [37]. Therefore, attraction and redispersion processes could be easily altered by using an external magnetic field, which showed great capability in the separability of $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ in the intended matrix.

Also, the pore structure of $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ was studied using N_2 adsorption-desorption; isotherm and pore size distribution are shown in Fig. 2D. A vertical increase under high relative pressures ($0.8 < P/P_0 < 1.0$) in the shape

of isotherm implied the presence of macropores. According to N_2 adsorption-desorption, the obtained isotherm was of type II and showed H3 type hysteresis loop [38]. The Brunauer-Emmett-Teller (BET) surface area and pore volume of the as-prepared composite were $153.19\text{ m}^2\text{ g}^{-1}$ and $0.924\text{ cm}^3\text{ g}^{-1}$, respectively. The results indicated that the surface area of $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ was adequate for the adsorption of BPA.

Optimization of MSPE Conditions

To achieve the optimal conditions for BPA extraction using the proposed nanoabsorbents, a series of experiments were designed and performed based on one-factor-at-a-time approach. The parameters influencing MSPE efficiency were the amount of adsorbent, extraction time, desorption solvent, and desorption volume. All experiments were carried out in triplicate.

Effect of solution pH. Generally, organic extraction solvent has a strong tendency for analytes existing in molecular forms. The influence of sample pH on the extraction of BPA was studied with pH value changing in the range of 2-9. As displayed in Fig. 3A, the obtained peak area of BPA was enhanced when sample pH was varied from 2 to 6. BPA is a weakly acidic compound with pK_a in the range of 9.6-10.2 [39] and exists in a molecular form at $\text{pH} < 9.6$. On the other hand, the results indicated higher extraction efficiency in the pH range of 4-6. In fact, in both acidic and alkaline solutions, favorable extraction was not performed, which could be due to the hydrolysis and degradation of BPA [40]. The hydrophobic interactions and hydrogen bonds between BPA and the amine groups of adsorbent might be responsible for the high extraction efficiencies observed in the pH range of 3-8 [41]. Nevertheless, the drop observed at pH 8 could be explained by the fact that when the difference between pH and pK_a was less than 2 units, BPA began to dissociate and partially existed in anionic form. Therefore, pH 6 was chosen as the optimum condition for the extraction of BPA by the as-prepared composite.

The effects of the amount of adsorbent and sample volume. The effect of sorbent amounts on BPA extraction efficiency was evaluated by dispersing various amounts of $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ adsorbent (25, 50, 100, 150, 200 and 300 mg in 25 ml standard solution). The obtained

results (Fig. 3B) demonstrated that the peak areas of BPA were increased as the amounts of adsorbent was increased from 25 to 150 mg, while further increase of sorbent amount had almost no effect. Therefore, 150 mg $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ was used in all subsequent experiments. To evaluate the effect of sample volume on the efficiency of the proposed methods, sample volumes of 5 to 100 ml were selected. The results showed that extraction efficiency was maximum at sample volume of 25 ml and at 50 ml sample volume, it was higher than 88%

(>88%). At higher sample volumes (data not shown), extraction efficiency showed a considerable decrease. Therefore, subsequent analyses were performed using 25 ml sample volume. Hence, a preconcentration factor of 50 was achieved with 25 ml sample volume of BPA and the final volume of 0.5 ml.

Effect of extraction time. For the optimization of extraction time, different contact times ranging from 1-15 min were applied to perform extraction process. Extraction time profile for BPA is shown in Fig. 3C. The

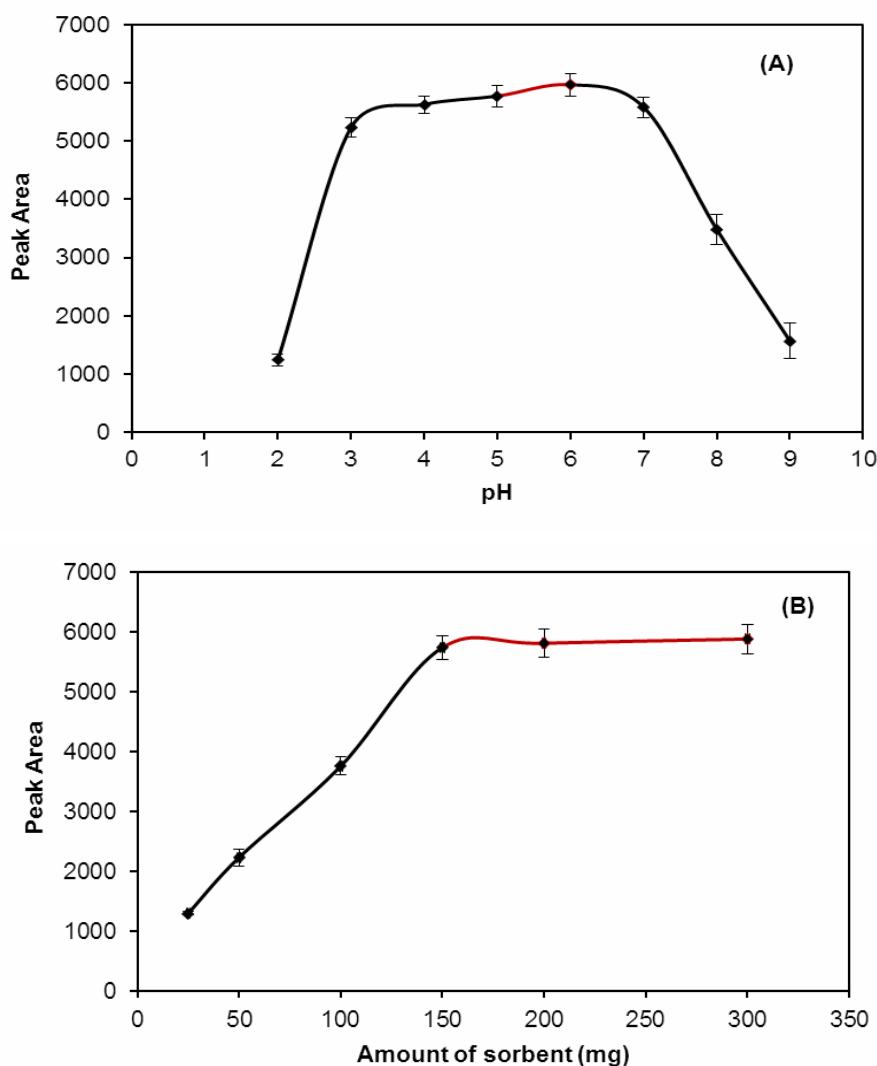


Fig. 3. Optimization of (A) sample pH, (B) magnetic sorbent amount, (C) extraction time and (D) desorption solvent.

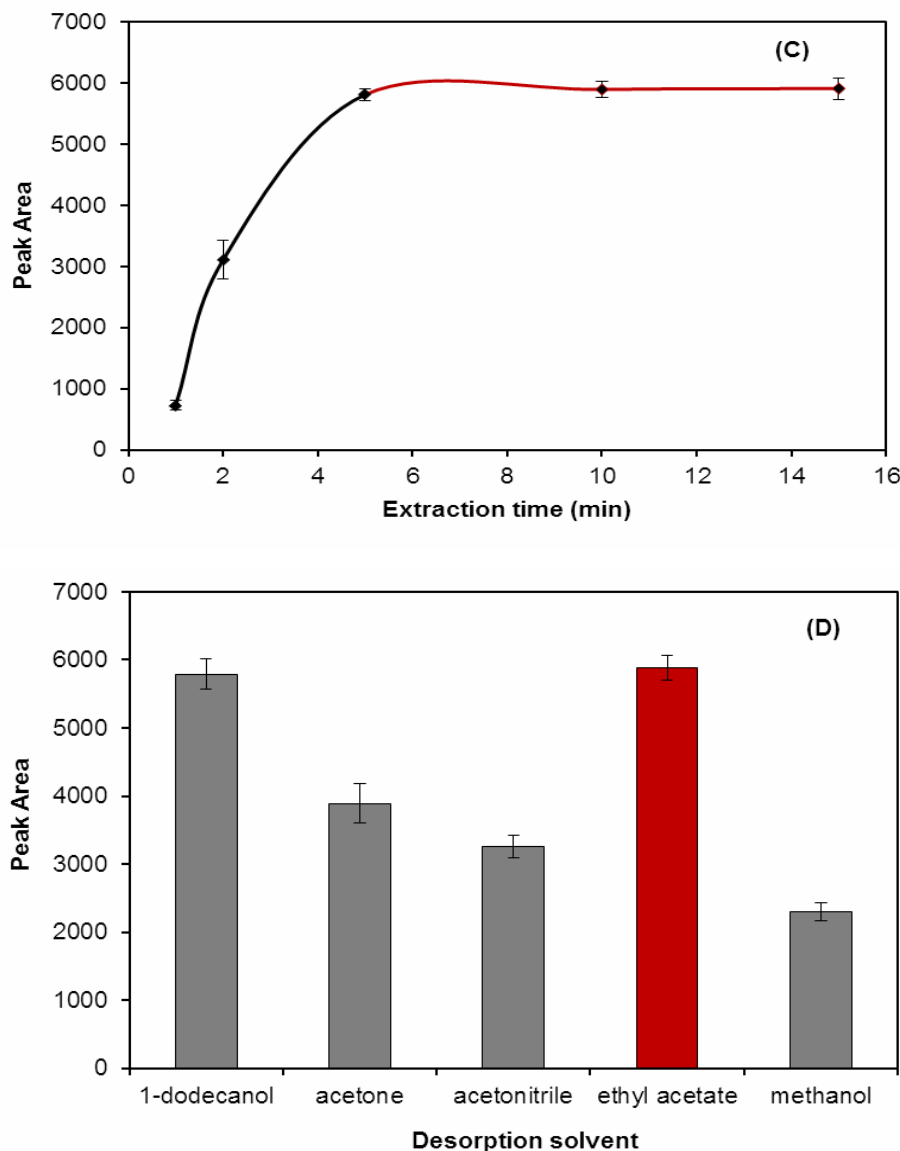


Fig. 3. Continued.

results demonstrated that 5 min was enough to capture the analyte from the solution. The results also demonstrated that 5 min was adequate to load analyte on sorbent. There was no significant enhancement in peak areas with prolonged extraction time. Rapid and strong interaction between the adsorbent and analyte significantly illustrated the efficiency of the proposed method. Therefore, extraction using 150 mg $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ composite within 5 min was applied for the following experiments.

Desorption condition. In the next step, the selection of appropriate solvent as an extractant phase was performed by the comparison of the performance of five solvents including 1-dodecanol, acetonitrile, acetone, methanol, and ethyl acetate in desorption process. Among the tested elution solvents, ethyl acetate achieved higher elution efficiencies and was accepted as eluent for further experiments (Fig. 3D).

In terms of the optimization of extractant volume,

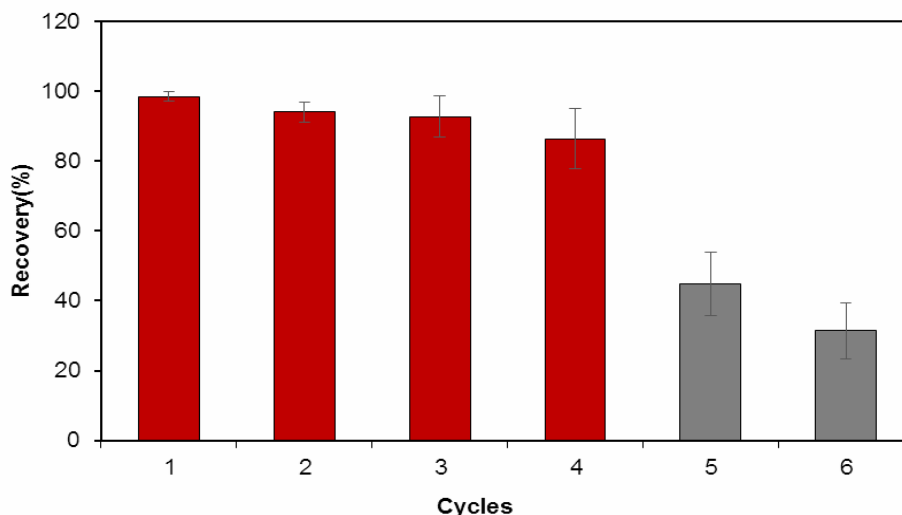


Fig. 4. The reusability of $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ nanocomposite after four successive uses.

although higher volumes of eluent facilitated the desorption of analyte from adsorbent, it weakened enrichment and analytical characteristics. By performing experiments using 50 to 350 μl solvent, it was found that 200 μl desorption solvent was sufficient to desorb BPA from sorbent. Finally, 200 μl ethyl acetate was employed in subsequent experiments.

Moreover, ultra-sonication facilitated the elution of analyte from sorbent. The effect of elution time on desorption efficiency was investigated with varying elution time from 1 to 20 min, where it was observed that 1 min was enough for BPA to be desorbed in 200 μl eluent (data not shown).

Reusability of the adsorbent. To evaluate the reusability of the as-prepared $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ composite, recycling experiments were performed in six consecutive separations-desorption cycles under the optimal experimental conditions. After each step, the isolated sorbent was washed with ethyl acetate solution (3 ml, three times) and rinsed with water thoroughly. The washed $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ was air-dried at room temperature and used directly in the following step under the same conditions. As shown in Fig. 4, it became evident that extraction recovery for up to four uses was $>85\%$, indicating that the prepared MOF nanocomposites were reusable and stable solid phase sorbents for the extraction of

BPA.

Evaluation of Method Performance

In order to evaluate the performance and reliability of the proposed method, analytical characteristic data was assessed under the optimized conditions and the calculated data are summarized in Table 2. In this study, calibration curves were depicted for six spiking levels of BPA standard in the concentrations range of 0.1-20 ng ml^{-1} . The equation regression for target analyte was $A = 3324 C + 558.5$ (A = analyte peak area, C = analyte concentration, ng ml^{-1}) with high correlation coefficient ($R^2 = 0.9967$). The limit of detection (LOD) and limit of quantification (LOQ) concentrations were estimated to be 0.03 and 0.1 ng ml^{-1} , respectively, when signal-to-noise ratios (S/N) was 3 and 10, respectively.

Also, repeatability was evaluated by determining RSD for five equal extractions of standard samples at the concentration of 1.0 ng ml^{-1} BPA. Since the obtained RSD value was lower than 6.5%, it could be concluded that MSPE method using $\text{Fe}_3\text{O}_4\text{-NH}_2\text{@MOF-235}$ composite presented high-performance characteristics and acceptable analytical figures of merits for extraction procedure to monitor BPA in mineral water samples. Besides, the calculated preconcentration factor of 50 for target analyte was obtained as a ratio between the volume of sample

Table 2. Regression Line and Quantitative Characteristics for the Developed Method

Compound	Linear regression				LOQ	LOD
	Slope	Intercept	R ² value ^a	LDR ^b	(ng ml ⁻¹) ^c	(ng ml ⁻¹) ^d
BPA	3324 ± 68	558.5 ± 112.2	0.9967	0.1-20	0.1	0.03

^aCorrelation coefficient. ^bLinear dynamic range (ng ml⁻¹). ^cLimit of quantification. ^dLimit of detection.

Table 3. Characteristics of the Examined Water Bottles

Characteristics	Bottled water brand				
	1	2	3	4	5
Bottled color	Clear	Clear	Clear	Light blue	Light blue
Bottle volume (ml)	300	300	1500	300	1500
pH	7.3	7.02	6.95	7.25	7.41

Table 4. Determination of BPA in Different Water Samples

Sample	Concentration of	Added BPA	Found BPA	Intra-day ^a	Found BPA	Inter-day ^b
	BPA (ng ml ⁻¹)			(ng ml ⁻¹)		Precision (RSD%)
Brand1	n.d. ^c	1.0	0.92	0.11	0.91	0.22
	n.d. ^c	5.0	4.92	0.28	4.83	0.36
	n.d. ^c	20	19.21	2.15	18.99	3.12
Brand2	n.d. ^c	1.0	0.93	0.10	0.89	0.19
	n.d. ^c	5.0	4.93	0.21	4.85	0.18
	n.d. ^c	20	19.42	1.96	19.83	3.44
Brand3	n.d. ^c	1.0	0.91	0.15	0.87	0.17
	n.d. ^c	5.0	4.89	1.03	4.86	0.24
	n.d. ^c	20	18.73	2.34	19.02	3.05
Brand4	n.d. ^c	1.0	0.92	0.16	1.01	0.08
	n.d. ^c	5.0	4.91	0.35	4.77	0.62
	n.d. ^c	20	18.92	2.55	19.41	3.31
Brand5	n.d. ^c	1.0	0.98	0.11	0.91	0.41
	n.d. ^c	5.0	4.91	0.35	4.80	0.37
	n.d. ^c	20	19.71	3.15	19.46	2.19

^aNumber of replicates:3. ^bNumer of days:3. ^cn.d.: Not detected.

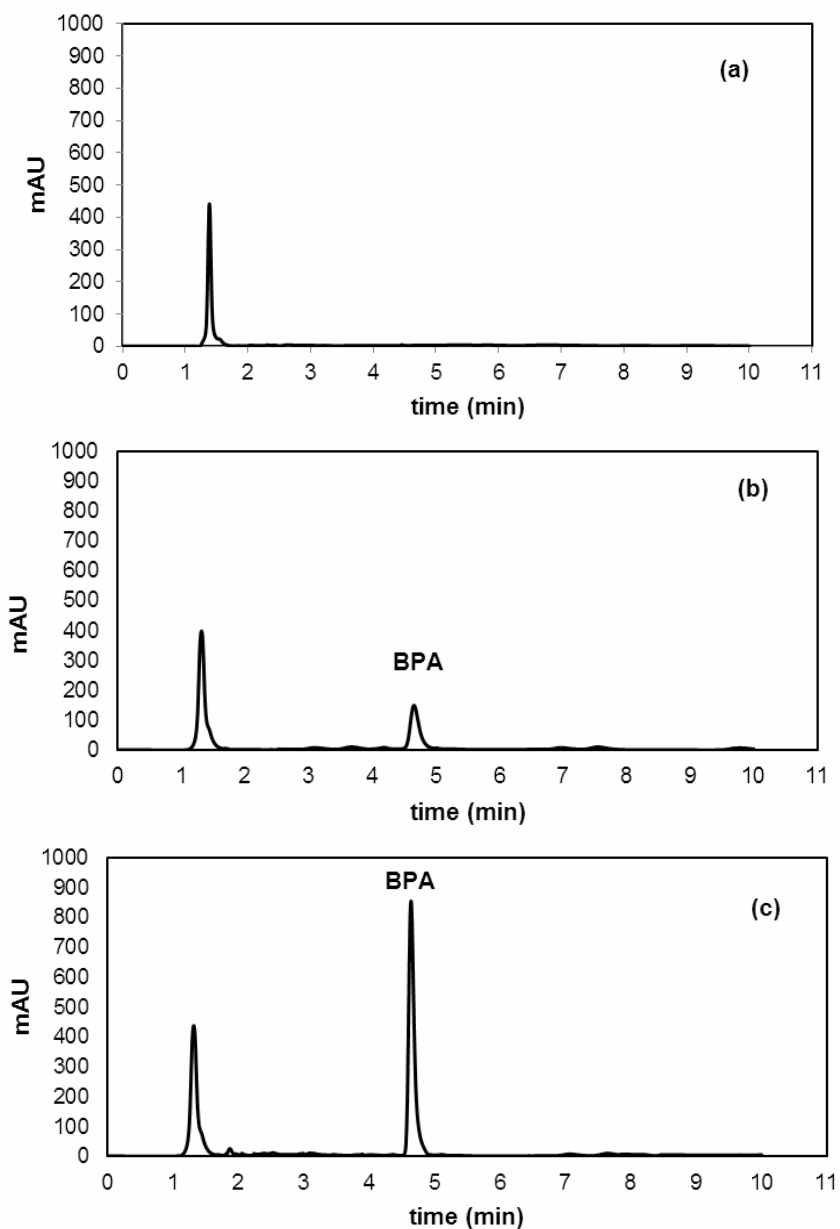


Fig. 5. The chromatograms obtained for brand1 water samples before (a) and after spiking with two different concentrations 1 (b) and 10 ng ml⁻¹ (c) of BPA, after MSPE under optimal conditions.

solution (25 ml) and the final volume (0.5 ml) obtained after elution step.

Real Water Analysis

Under the optimized conditions, BPA contents were evaluated in mineral water samples of 5 different brands

(labeled 1-5) produced in the winter of 2020 and randomly purchased from local supermarkets in Urmia, Iran. The entire sample bottles were made of polyethylene tetra phthalate (PET) and according to vendors, they were stored in dark at 20 °C. Table 3 shows the physical characteristics of the examined bottled water brands.

Water samples were determined using the proposed MSPE and HPLC. The obtained results indicated that all samples were free from BPA contamination. Therefore, spiked BPA standards were utilized to evaluate matrix effects. Figure 5 shows the chromatograms depicted for brand 1 water samples before and after spiking with two different concentrations of BPA (1 and 10 ng ml⁻¹).

Also, the precisions (intra-day and inter-day) of the proposed method for water samples are tabulated in Table 4. The extraction recoveries of the proposed method for spiked samples were 91%-99% (n = 3) (data not shown in the table). As can be seen in Table 4, satisfactory results were obtained and these values fall in acceptable range for such real samples. Therefore, experimental results demonstrated that the matrices of environmental water samples did not have significant effects on the determination of BPA in water.

CONCLUSIONS

In the present study, we investigated the potential application of a magnetic metal-organic framework structure as a sorbent for the microextraction and preconcentration of BPA in some bottled mineral waters. Characterization of superparamagnetic composite was performed using several techniques. Besides, the proposed sorbent showed high durability and reusability (for at least four separation-desorption cycles) and could be used several times without measurable performance loss. The optimal conditions for separation with the highest efficiency were determined as follows, extraction time: 5 min, sample pH value: 6, the mass of sorbent: 150 mg, extractant solvent, and volume: 200 µl ethyl acetate. The method showed linear response over the concentration range of 0.1-20 ng ml⁻¹ with LOD and LOQ values of 0.03 ng ml⁻¹ and 0.1 ng ml⁻¹, respectively, for the studied analytes. Based on the obtained data, high-performance microextraction of BPA from bottled mineral water samples could be carried out using Fe₃O₄-NH₂@MOF-235 composite.

ACKNOWLEDGMENTS

Islamic Azad University, Tabriz Branch, Faculty of Science, Laboratory of chemistry supported this work.

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