



# A nanosized magnetic metal-organic framework of type MIL-53(Fe) as an efficient sorbent for coextraction of phenols and anilines prior to their quantitation by HPLC

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## Abstract

The authors describe the synthesis of a magnetic metal-organic framework (MOF) of type MIL-53(Fe) for coextraction of phenols and anilines from various environmental samples. A quick method for dispersive micro-solid phase extraction (D- $\mu$ -SPE) was developed for coextraction of the analytes 4-nitrophenol (4-NP), 4-chlorophenol (4-CP), 4-chloroaniline (4-CA), 1-amino-2-naphthol (1-A2N) and 2, 4-dichloroaniline (2, 4-DCA). The MOF was characterized by SEM, TEM, FT-IR, EDS, thermogravimetry, VSM and XRD. The method was optimized by response surface methodology combined with desirability function approach, specifically with respect to pH value of the sample, amount of sorbent, sorption time, salt concentration, sample volume, type and volume of the eluent, and elution time. Following elution with acetonitrile, the analytes were quantified by HPLC with photodiode array detection. Responses are linear in 0.1–2000  $\mu\text{g}\cdot\text{L}^{-1}$  concentration ranges. The limits of detection and relative standard deviations (for  $n = 5$ ) are in the range of 0.03–0.2  $\mu\text{g}\cdot\text{L}^{-1}$  and 3.5–12.6%, respectively. Enrichment factors are 113, 61, 87, 144 and 114 for 4-NP, 4-CP, 4-CA, 1-A2N and 2,4-DCA, respectively. Recoveries from spiked samples ranged from 39.5 to 93.3%. The magnetic sorbent was successfully applied to the coextraction and determination of the analytes in river, rain and hookah water samples.

**Keywords** Magnetic sorbent · Dispersive micro-solid phase extraction · Pollutants · Desirability function · Water samples

## Introduction

Phenols and anilines even at trace levels of concentration are suspected to be carcinogenic [1–3]. Thereby, it is extremely momentous to extend a sensitive, accurate and environmentally friendly determination method for measurement of these pollutants. Chloroanilines (CAs) and phenolic compounds are used in different industrial processes like pharmaceuticals,

synthesis of chemical compounds like dyes or some pesticides, plastics and using them as reagents [1, 2, 4, 5]. Therefore, they can be discovered in waters, soils, and sediments [6–8]. Among these compounds, *p*-nitrophenol and 1-amino-2-naphthol can have irreparable harmful effects on the health of humans and animals. *p*-nitrophenol damages mitochondria and prevents energy metabolism in human and animals [9]. 1-amino-2-naphthol causes bladder tumors creation after bladder insemination, made by the reduction of Orange II [10]. Different analytical techniques such as high-performance liquid chromatography (HPLC) with photo diode array detection (PDA) [11], electrochemical detection [12], or mass spectrometry (MS) [13], gas chromatography (GC) with flame ionization detection (FID) [14], capillary electrophoresis (CE) with amperometric detection [3], have been applied to quantification of phenols, anilines and compounds derived from them.

Sample preparation is an essential step prior to the determination of these compounds in different samples [2, 15, 16]. D- $\mu$ -SPE is a well-established sample pretreatment method

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for both cleaning up samples and preconcentrating in a variety of matrices. This method boasts of high versatility due to the great diversity of solids accessible, covering a wide range of chemical functionalities [17, 18].

Micro or nano sorbents showing a dramatically larger surface area with shorter diffusion path in comparison with other sorbents [19]. Magnetic nanoparticles (MNPs) are member of this group of sorbents, they can disperse homogenously in the sample solution and separate by helping of an external magnet [3, 11, 20, 21]. MOFs, are a marvelous multifunctional inorganic-organic materials with various holes and functionalized 3D crystalline structures that formed by linkers and metal ions [22–25]. MOFs have interesting unique attributes like high surface area, high pore volume, adjustable porous sizes and chemical tenability. These attributes make MOFs applicable in many field such as materials with magnetic properties, separation, drug delivery and heterogeneous catalysis, gas storage and purification, luminescent properties, chemical sensing [24–26]. MIL-53(Fe), a Fe-based MOFs, has a three-dimensional porous structure with unlimited one-dimensional linkage of  $-\text{Fe}-\text{O}-\text{O}-\text{Fe}-\text{O}-\text{Fe}-$ , cross-linked by terephthalic acid (1, 4-BDC) as a linker [27]. According to the features given, magnetic MOFs are an ideal sorbent in D- $\mu$ -SPE method. We report the synthesis of a new high performance MOF [ $\text{Fe}_3\text{O}_4$ @MIL-53(Fe)] with entire characterization and confirmation of it. This MOF was used for coextraction of [4-nitrophenol (4-NP), 4-chlorophenol (4-CP), 4-chloroaniline (4-CA), 2, 4-dichloroaniline (2, 4-DCA) and 1-amino-2-naphtol (1-A2N)] based on D- $\mu$ -SPE method prior to their quantitation by HPLC. The synthesized magnetic MIL-53(Fe) has core-shell nanostructure with  $\text{Fe}_3\text{O}_4$  core, which speeds up isolation of nanosorbent from the sample solution. The experimental results showed that magnetic MIL-53(Fe) have a high sorption capacity for intended analytes. This is because of the existence of some probably interactions like  $\pi$ -interaction, hydrophobic and hydrogen bonding between the intended analytes and the sorbent and cavities in MOF structure that can capture the intended analytes.

## Experimental

### Chemicals and reagents

HPLC grade acetonitrile and methanol were procured from Daejun (Seoul, South Korea, [www.daejungchem.co.kr](http://www.daejungchem.co.kr)). 1, 4-BDC,  $\text{FeCl}_3$ ,  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ , ammonium hydroxide (28% w.v<sup>-1</sup>), NaOH, HCl, NaCl, *N, N*-dimethyl formamide (DMF), 2-propanol, and acetone that all of these chemicals

were of analytical grade were provided by Merck (Darmstadt, Germany, [www.merck-chemicals.com](http://www.merck-chemicals.com)). Ultrapure purity water obtained from a milli-Q system (Millipore, Bedford, MA, USA; [www.emdmillipore.com](http://www.emdmillipore.com)) was used all over the experiments. 4-NP ( $\log P = 1.61$ ,  $\text{pK}_a = 7.07$ ), 4-CP ( $\log P = 2.27$ ,  $\text{pK}_a = 9.96$ ), 4-CA ( $\log P = 1.75$ ,  $\text{pK}_b = 3.49$ ), 1-A2N ( $\log P = 1.83$ ,  $\text{pK}_b = 4.16$ ,  $\text{pK}_a = 10.13$ ) and 2, 4-DCA ( $\log P = 2.35$ ,  $\text{pK}_b = 1.98$ ) were purchased from Sigma-Aldrich (Milwaukee, WI, USA, [www.sigmaaldrich.com](http://www.sigmaaldrich.com)).

### Preparation of the samples and standards

Stock standard solutions of 4-NP, 4-CP, 4-CA, 1-A2N and 2, 4-DCA at a concentration of 1000 mg·L<sup>-1</sup> were prepared in methanol. The working standard solutions were prepared daily dilution of the stock solution. Three different water samples (Hookah water, river water and rain water) were investigated for determination of intended analytes. Hookah water sample (five-time used) was obtained from a hookah lounge. River water sample was collected from Karaj River (Karaj, Iran). Rain water sample was collected during March 2018 (Tehran, Iran). 20 mL of each sample (spiked/non-spiked) was used without any dilution.

### Instrumentation

The chromatographic analyses were conducted on a Shimadzu HPLC instrument model SCL-10AVP (Tokyo, Japan, [www.shimadzu.com](http://www.shimadzu.com)), consisting of a LC-10AVP pump, SPD-M10AVP photo diode array (PDA) detector, and a Rheodyne7725i (PerkinElmer, USA, [www.perkinelmer.com](http://www.perkinelmer.com)). A 100  $\mu\text{L}$  sample loop and 250  $\mu\text{L}$  Hamilton HPLC syringe (Reno, NV, USA, [www.hamiltoncompany.com](http://www.hamiltoncompany.com)) were used too. Data analysis was performed using LC-solution software. A Knauer HPLC column (Vertex Plus Column, Germany, [www.knauer.net](http://www.knauer.net), 250 mm  $\times$  4.6 mm, i.d. 5  $\mu\text{m}$ ) consisting a C<sub>18</sub> precolumn for protecting was employed for all separations, under an isocratic program using 50% acetonitrile and 50% water as mobile phase ingredients. Also, the flow rate was set at 1 mL·min<sup>-1</sup> and the monitoring wavelength was 315 nm for 4-NP, 230 nm for 4-CP, 240 nm for 4-CA and 1-A2N and 245 nm for 2, 4-DCA. Under this condition, the retention time of 4-NP, 4-CP, 4-CA, 1-A2N and 2, 4-DCA was 5.1, 7.2, 8.4, 10.6 and 16.5 min, respectively. A digital pH meter (Metrohm, [www.metrohm.com](http://www.metrohm.com), model 827, with a glass calomel electrode) was utilized for measuring of pH values. Vortex mixing was accomplished with a MS3 digital vortex agitator (IKA Company, Staufen, Germany, [www.ika.com](http://www.ika.com)). A 25 mL sample vial, a MR 3001 heating-magnetic stirrer

(Heidolph Company, Kelheim, Germany, [www.heidolph-instruments.com](http://www.heidolph-instruments.com)) were employed in extraction process. For characterization of magnetic MOF (MMOF), an EM 3200 KYKY scanning electron microscope (SEM, Zhongguancun, Beijing, China, [www.kyky.com.cn](http://www.kyky.com.cn)) was used for morphological evaluation. Transmission electron microscopy (TEM) was performed on a Zeiss EM900 instrument at 150 kV (Carl Zeiss, Germany, [www.zeiss.com](http://www.zeiss.com)). XRD patterns were recorded on a powder X-ray diffractometer (Philips-PW 12C, Amsterdam, the Netherlands; [www.innovationsservices.philips.com](http://www.innovationsservices.philips.com)) armed with a Cu K $\alpha$  radiation source. A VEGAII TESCAN instrument ([www.tescan.com](http://www.tescan.com)) was employed for accomplishing the energy dispersive X-ray spectroscopy (EDX). Fourier transform infrared (FT-IR) spectrometer (Bruker IFS-66 FT-IR, Bruker Optics, Karlsruhe, Germany, [www.brukeroptics.com](http://www.brukeroptics.com)) was applied to examine the infrared spectra of MOF and MMOF using a pressed KBr tablet. Thermogravimetric analysis (TGA) was done on a Bahr STA-503 (Bahr-Thermoanalyse GmbH, Hüllhorst, Germany; [www.tainstruments.com](http://www.tainstruments.com)) instrument under air atmosphere. Magnetic measurements of the products were conducted with a vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir Co.; Kashaan Kavir; Iran; [www.mdk-magnetics.com](http://www.mdk-magnetics.com)) at chamber temperature in a 1 Tesla magnetic field. For the purpose of sorbent collection and magnetic decantation an Nd-Fe-B strong magnet (15 cm  $\times$  12 cm  $\times$  5 cm, 1.4 T) was used.

### Synthesis of magnetic MIL-53(Fe)

Fe<sub>3</sub>O<sub>4</sub> NPs were synthesized by chemical co-precipitation method [17, 19, 28]. The Fe<sub>3</sub>O<sub>4</sub>@MIL-53(Fe) was synthesized via solvothermal method according to the literature with slight modifications [29]. The preparation steps of Fe<sub>3</sub>O<sub>4</sub> NPs and Fe<sub>3</sub>O<sub>4</sub>@MIL-53(Fe) are described in detail in the Electronic Supplementary Material and Fig. 1S.

### Synthesis of MIL-53(Fe)

The synthesis of MIL-53(Fe) is similar to the Fe<sub>3</sub>O<sub>4</sub>@MIL-53(Fe) preparation process, the only difference is the lack of Fe<sub>3</sub>O<sub>4</sub> NPs in synthesis procedure.

### Fe<sub>3</sub>O<sub>4</sub>@MIL-53(Fe) based D- $\mu$ -SPE procedure

First, 20 mL solution of the intended analytes (1.0 mg L<sup>-1</sup>) that containing 15% (w·v<sup>-1</sup>) NaCl was placed into the 25 mL sample vial and 20 mg Fe<sub>3</sub>O<sub>4</sub>@MIL-53(Fe) was appended to the vial. Then, sample solution pH was set to 5.0. The mixture was stirred for 8.0 min at 1250 rpm. Afterward, a strong external magnet was

used for quickly collection of sorbent from the sample solution. When the suspension became lucid, the supernatant was decanted and the collected sorbent was eluted with 130  $\mu$ L of acetonitrile by vortexing for 2.0 min with the purpose of desorbing the pre-concentrated intended analytes. Finally, for analyzing the intended analytes, the eluate was injected into the HPLC-PDA.

### Zero charge (pH<sub>PZC</sub>) determination

In several beakers, a known amount (10 mg) of Fe<sub>3</sub>O<sub>4</sub>@MIL-53(Fe) was dispersed in 10 mL of the degassed 0.01 M NaNO<sub>3</sub> aqueous solution at 25 °C. The sample solutions pH was set at 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 using aqueous 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> or 0.1 mol L<sup>-1</sup> NaOH solutions as proper. This suspension was stirred for 24 h at 25 °C, after this time the pH of each beaker was measured. Finally, a plot of the primary solutions pH against  $\Delta$ pH (differences between the primary and the final solutions pH) of the solutions gives the pH<sub>PZC</sub> value for the sample. The pH<sub>PZC</sub> related to the pH where  $\Delta$ pH = 0 [5, 30].

### Multivariate optimization

For optimizing the parameters that effect on D- $\mu$ -SPE, central composite design (CCD) was utilized by employing Design-Expert 7.0.0 (trial version) software.

## Results and discussion

### Choice of material

Among diverse materials which can be used as D- $\mu$ -SPE sorbents, such as GO, Fe<sub>3</sub>O<sub>4</sub>@GO, RGO, CNTs, Fe<sub>3</sub>O<sub>4</sub>@CNTs, RCNTs, MOFs and Fe<sub>3</sub>O<sub>4</sub>@MOFs, Fe<sub>3</sub>O<sub>4</sub>@MOF was selected owing to its considerable properties. MIL-53(Fe) has a porous structure that can capture the analytes, resulted in the great increase of specific surface area and also due to the attendance of aromatic rings, hydroxyl groups and metal centers (Fe) in its structure, no modification is required. In spite of the fact that the other sorbents, should be modified to be able to interact with the analytes. Moreover, the duration of synthesis of MIL-53(Fe) is very short (2 h) compared to other sorbents. The attendance of Fe<sub>3</sub>O<sub>4</sub> nanoparticles in MIL-53(Fe) structure, increases the stability of the MIL-53(Fe) and also facilitates the separation of this sorbent from the sample solution compared to non-magnetic sorbent such as GO, RGO, CNTs and RCNTs. Based on the diverse functional moieties, this sorbent has a potential applicability for the extraction of other analytes like pesticides, drugs, PAHs and any

other pollutants in samples with complex matrix. The only limitation of this method is that the synthesized sorbent is non-selective. This problem can be resolved by optimization of the extraction conditions (such as pH of sample, salt concentration etc.) or by sorbent modification.

### Characterization studies

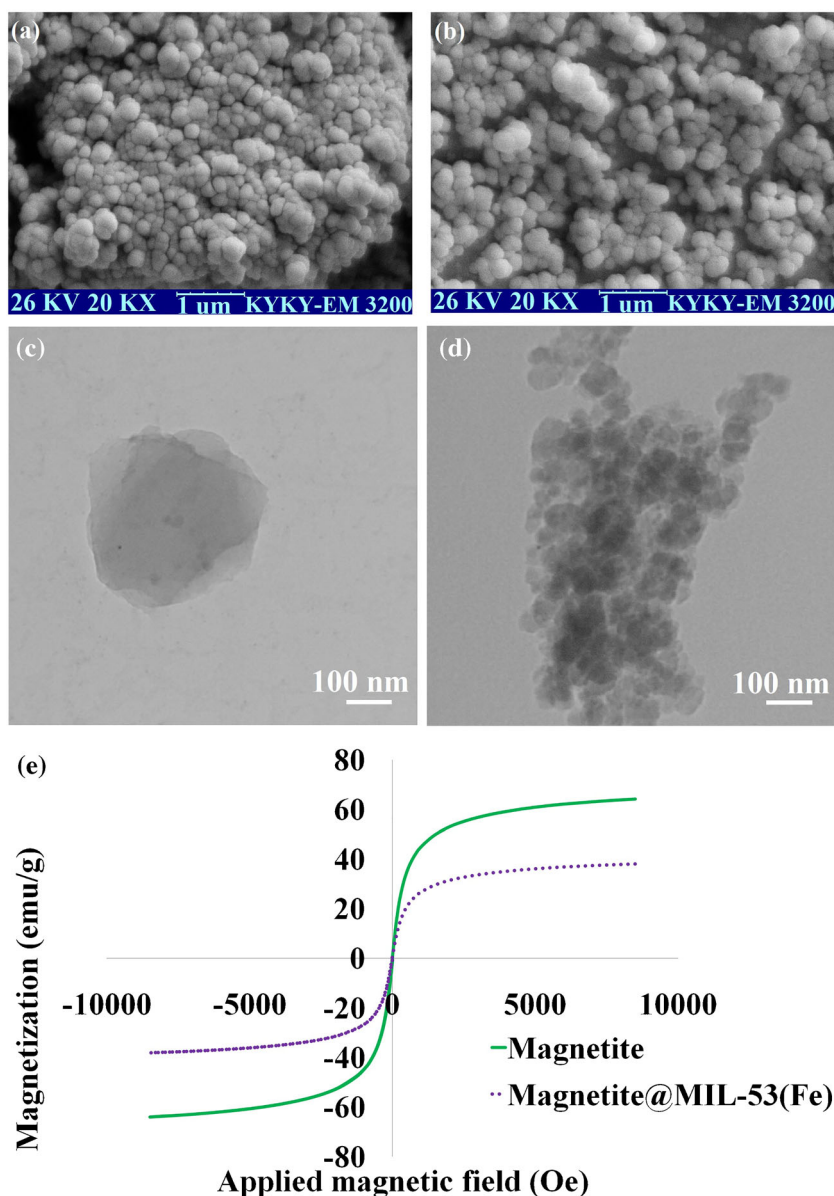
The FT-IR, EDX, XRD, TGA and zeta-potential measurements information related to characterization of the sorbent are described in the Electronic Supplementary Materials (Fig. 2S–6S).

The SEM and TEM methods were utilized to explore the morphology of MIL-53(Fe) and magnetic MIL-53(Fe) (Fig.

1). As illustrated in Fig. 1a, the MIL-53(Fe) crystals have an average size of about 100 nm ( $n = 50$  particles). Figure 1b shows the SEM image of the synthesized magnetic MIL-53(Fe). It is demonstrated that the sizes of magnetic MIL-53(Fe) crystals are obviously increased about 170 nm ( $n = 50$  particles) than the MIL-53(Fe) crystals owing to the incorporation of  $\text{Fe}_3\text{O}_4$  nanoparticles into the MIL-53(Fe) pores. Figure 1c displays the TEM image of MIL-53(Fe). TEM image shown in Fig. 1d reveals clearly that the  $\text{Fe}_3\text{O}_4$ @MIL-53(Fe) crystals are core-shell structures with  $\text{Fe}_3\text{O}_4$  cores and MIL-53(Fe) shell with an average size of 40 nm ( $n = 10$  particles) for  $\text{Fe}_3\text{O}_4$  NPs.

The magnetic behavior of  $\text{Fe}_3\text{O}_4$  NPs and  $\text{Fe}_3\text{O}_4$ @MIL-53(Fe) composite were studied and the VSM plots are illustrated in Fig. 1e. As illustrates in Fig. 1e, the

**Fig. 1** SEM images of (a) MIL-53(Fe) and (b)  $\text{Fe}_3\text{O}_4$ @MIL-53(Fe), TEM images of (c) MIL-53(Fe) and (d)  $\text{Fe}_3\text{O}_4$ @MIL-53(Fe), and VSM plots of (e)  $\text{Fe}_3\text{O}_4$  NPs and  $\text{Fe}_3\text{O}_4$ @MIL-53(Fe)



**Table 1** Analytical parameters of the Fe<sub>3</sub>O<sub>4</sub>@MIL-53(Fe) based D-μ-SPE-HPLC method

Analyte	LOD (μg·L <sup>-1</sup> )	LDR (μg·L <sup>-1</sup> )	Regression equation	R <sup>2</sup>	EF <sup>b</sup>	ER <sup>c</sup> (%)	RSD (%) <sup>d</sup> Within-day				RSD (%) <sup>d</sup> Between-day			
							50 <sup>a</sup>	100 <sup>a</sup>	250 <sup>a</sup>	500 <sup>a</sup>	50 <sup>a</sup>	100 <sup>a</sup>	250 <sup>a</sup>	500 <sup>a</sup>
4-NP	0.03	0.1–2000	y = 439246 c <sup>a</sup> + 71200	0.9994	113.5	73.8	6.2	5.4	4.7	3.9	8.8	8.4	7.3	6.9
4-CP	0.2	0.5–2000	y = 86412 c + 16120	0.9994	60.8	39.5	5.2	4.8	4.4	3.5	9.1	8.6	8.1	7.4
4-CA	0.15	0.5–2000	y = 166670 c + 35787	0.9994	87.4	56.8	5.1	4.9	4.3	3.7	8.7	8.3	7.6	7.1
1-A2N	0.08	0.5–2000	y = 502751 c + 84311	0.9992	143.6	93.3	7.6	6.9	6.2	5.5	12.6	11.8	11.1	10.2
2, 4-DCA	0.1	0.5–2000	y = 439177 c + 46821	0.9995	113.8	74.0	7.2	6.6	5.9	5.2	11.9	11.1	10.3	9.6

<sup>a</sup> Concentration (μg·L<sup>-1</sup>)<sup>b</sup> Enrichment factor<sup>c</sup> Extraction recovery percentage<sup>d</sup> Relative standard deviation (*n* = 5 samples for within day and *n* = 3 days for between day)

saturation magnetization of Fe<sub>3</sub>O<sub>4</sub> NPs and Fe<sub>3</sub>O<sub>4</sub>@MIL-53(Fe) was 64 and 38 emu·g<sup>-1</sup> respectively, which depicts superparamagnetic properties of the sorbents and is enough for magnetic separation with a common magnetic field [11] (Fig. 1e).

### Optimization of the extraction condition

The following parameters were optimized: (a) sorbent type; (b); eluent type and its volume; (c) effect of ionic strength; (d) pH effect; (e) sample volume; (f) amount of the sorbent; (g) sorption time. Respective data and Figures are given in the Electronic Supporting Material (Fig. 7S–8S). In short, the following experimental conditions were found to give best results: (a) optimal sorbent: Fe<sub>3</sub>O<sub>4</sub>@MIL-53(Fe); (b) optimal eluent and its volume: acetonitrile, 130 μL; (c) optimal ionic strength:

15% (w·v<sup>-1</sup>) NaCl; (d) best sample pH value: 5.0; (e) sample volume: 20 mL; (f) amount of the sorbent: 20 mg; (g) sorption time: 8 min.

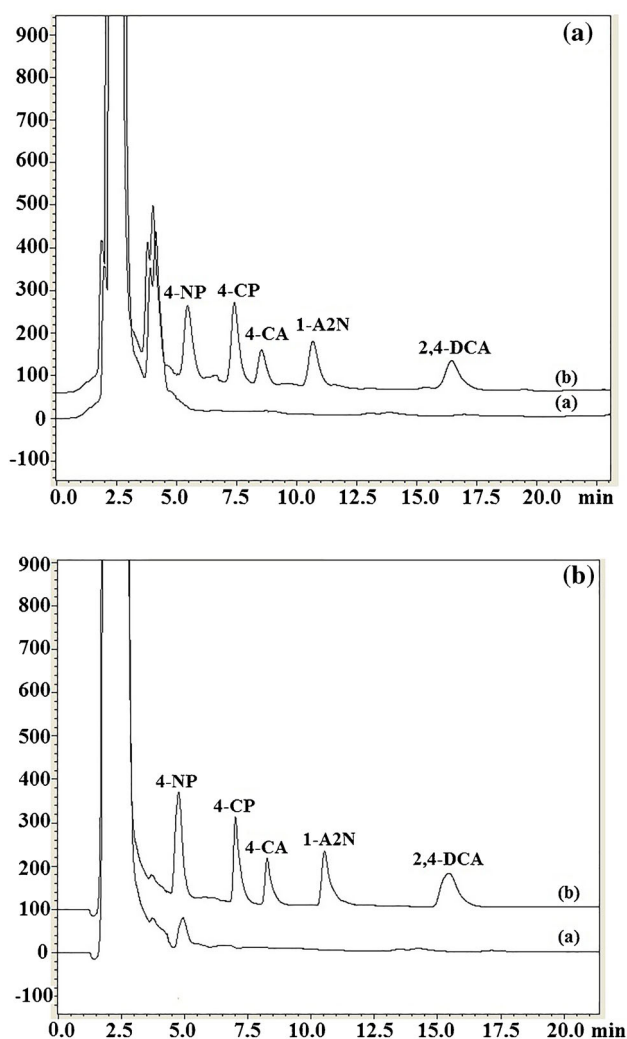
### Method analytical performance

Quantitative parameters of the D-μ-SPE-HPLC-PDA method, including the limits of detection (LODs), linear dynamic range (LDR), enrichment factors (EFs), and extraction recoveries (ER%) were determined, under the selected experimental conditions. The results are illustrated in Table 1. Excellent linearity with coefficients of determination higher than 0.999 were achieved for all the analytes. LODs and LOQs (limits of quantification) were calculated as 3 and 10 S/N (signal-to-noise), respectively. The EFs were computed as the ratio of the slopes of each analyte calibration plots before extraction and after extraction process. The repeatability and reproducibility of

**Table 2** Determination of the intended analytes in different water samples (*n* = 3)

Sample	Analyte	C <sub>added</sub> (μg·L <sup>-1</sup> )	C <sub>found</sub> ± SD (μg·L <sup>-1</sup> )	RR <sup>a</sup> (%)	RSD (%)
Hookah water five-time used	4-NP	-100	n.d. 98.3 ± 5.013	-98.3	-5.1
	4-CP	-100	n.d. 103 ± 4.429	-103	-4.3
	4-CA	-100	n.d. 96.0 ± 4.512	-96	-4.7
	1-A2N	-100	n.d. 99.1 ± 6.540	-99.1	-6.6
	2, 4-DCA	-100	n.d. 93.4 ± 5.977	-93.4	-6.4
River water	4-NP	-30	n.d. 30.9 ± 1.761	-103	-5.7
	4-CP	-30	n.d. 30.8 ± 1.509	-103	-4.9
	4-CA	-30	n.d. 28.8 ± 1.324	-96	-4.6
	1-A2N	-30	n.d. 30.2 ± 2.204	-101	-7.3
	2, 4-DCA	-30	n.d. 29.1 ± 2.066	-97	-7.1
Rain water	4-NP	-30	7.6 ± 0.501 38.2 ± 2.330	-102	6.6 6.1
	4-CP	-30	n.d. 28.5 ± 1.482	-95	-5.2
	4-CA	-30	n.d. 29.1 ± 1.455	-97	-5.0
	1-A2N	-30	n.d. 30.9 ± 2.379	-103	-7.7
	2, 4-DCA	-30	n.d. 29.8 ± 2.145	-96	-7.2





**Fig. 2** The chromatograms of (a) River water sample (a) before spiking, (b) spiked at  $30 \mu\text{g}\cdot\text{L}^{-1}$  of each analytes, and (b) Rain water sample (a) before spiking, (b) spiked at  $30 \mu\text{g}\cdot\text{L}^{-1}$  of each analytes after D- $\mu$ -SPE

the method (as RSD) were obtained by performing five replicate experiments at four levels of analytes concentration ( $50$ ,  $100$ ,  $250$  and  $500 \mu\text{g}\cdot\text{L}^{-1}$ ). The within day and between day RSDs of the mentioned method for determination of intended analytes are equal or less than  $3.7\%$  and  $9.6\%$ , respectively. The extraction recoveries percentage, which refers to a percentage of an efficient extraction of total analyte by the sorbent and eventually eluted with acetonitrile, are ranged from  $39.5$  to  $93.3\%$ . Combination of low detection limit with extensive linear range, providing a high potential for determination of the low concentration levels of intended analytes in water samples.

### Real samples analysis

To evaluate the applicability of the  $\text{Fe}_3\text{O}_4@\text{MIL-53}(\text{Fe})$  based D- $\mu$ -SPE-HPLC method on real samples, recovery studies were accomplished in water samples (rain water,

river water and hookah wastewater) under the selected experimental conditions. The results of the determination and recovery studies with three replicate for the non-spiked and spiked samples are demonstrated in Table 2. As can be beheld, the relative recoveries are ranged from of  $93.4$  to  $103.1\%$  with RSDs below  $8.1\%$ . Therefore, the results confirm that the mentioned method is accurate and repeatable for enrichment and determination of the low concentration levels of phenols and anilines in diverse water samples. Fig. 2 displays typical HPLC chromatograms of non-spiked and spiked rain water, river water and hookah wastewater sample after extraction under the opted conditions.

### Comparison of the D- $\mu$ -SPE-HPLC-PDA method with other reported approaches

Table 3 displays a comparison between the results achieved by this method and those achieved by some other formerly reported methods for coextraction and determination of 4-NP, 4-CP, 4-CA, 1-A2N and 2,4-DCA in various real samples. As can be beheld, the mentioned method indicated satisfactory wide linearity, acceptable RSDs and extraction recoveries compared with the reported methods. The achieved LODs of this study are lower than the other reported method. This method not only extracts phenols and anilines simultaneously at low concentration levels but also uses low amount of sorbent and little volume of organic solvents compared to the reported methods.

### Conclusion

$\text{Fe}_3\text{O}_4@\text{MIL-53}(\text{Fe})$  was synthesized and utilized as an efficient nanoadsorbent for coextraction of phenols and anilines as pollutants at low concentration levels in diverse water samples. The synthesized  $\text{Fe}_3\text{O}_4@\text{MIL-53}(\text{Fe})$  has core-shell structure with  $\text{Fe}_3\text{O}_4$  cores and MIL-53(Fe) shell. The presence of  $\text{Fe}_3\text{O}_4$  NPs in MIL-53(Fe) structure, makes the  $\text{Fe}_3\text{O}_4@\text{MIL-53}(\text{Fe})$  structure more stable than MIL-53(Fe) without  $\text{Fe}_3\text{O}_4$  NPs attendance and also helps to collect this sorbent from sample solution easily by a strong external magnet. This study introduces an efficient and environmentally friendly method which provides limits of detection in the low range and acceptable extraction recoveries and manifests the high potential of this method for applying in sample preparation step. Moreover, the duration of synthesis of MIL-53(Fe) is very short ( $2$  h) compared to other sorbents. Based on the diverse functional moieties, this sorbent has a potential applicability for the extraction of other analytes like pesticides, drugs, PAHs and any other pollutants in samples with complex matrix. The only limitation of this method is that the synthesized sorbent is non-selective. This problem can be resolved by optimization of the extraction

**Table 3** Comparison of the Fe<sub>3</sub>O<sub>4</sub>@MIL-53(Fe) based D-μ-SPE-HPLC method with other reported method for the extraction and determination of 4-NP, 4-CP, 4-CA, 1-A2N and 2, 4-DCA

Analytes	Sample	Method	LDR	LOD	Extraction time (min)	RSD (%)	Ref.
4-NP	Pond, river, and urban wastewater	SMS-LLME <sup>a</sup> -HPLC-UV	2.0–1000	0.26	30	5.85	[2]
2, 4-DCA	River water	HFBLPME-GC-FID <sup>b</sup>	6.6–1000	2.2	20	12.4	[1]
4-CA, 1-A2N	River water, surface water, wastewater, snow water	VAILME-UFLC <sup>c</sup> -UV	1.6–200	0.24–0.39	2	≤ 5.3	[6]
4-NP, 4-CP, 2, 4-DCA	Rain, snow and river Water	D-μ-SPE-HPLC-DAD	0.25–500	0.05–0.1	12	≤ 6.5	[11]
4-NP	Surface seawater	LLLME-CLC <sup>d</sup>	1–200	0.5	50	2.03	[15]
4-NP, 1-A2N, 2, 4-DCA	Rain, snow and river Water	D-μ-SPE-HPLV-DAD	0.5–400	0.1–0.2	7.5	≤ 8.5	[31]
4-CA	Tap water, wastewaters, river water	EC-in-tube SPME <sup>e</sup> -HPLC-UV	0.5–100	0.3	25	5.5	[32]
4-NP, 4-CP, 4-CA, 1-A2N, 2, 4-DCA	Hookah wastewater, river water and rain water	D-μ-SPE-HPLC-DAD	0.1–2000	0.03–0.2	10	≤ 3.5	Current method

All concentrations are based on μg·L<sup>-1</sup>

<sup>a</sup>Supramolecular solvent liquid–liquid microextraction

<sup>b</sup>Hollow fiber-based liquid phase microextraction-gas chromatography-flame ionization detector

<sup>c</sup>Vortex-assisted ionic liquid microextraction-ultra fast liquid chromatography

<sup>d</sup>liquid–liquid–liquid microextraction-capillary liquid chromatography

<sup>e</sup>On-line electrochemically controlled in-tube solid-phase microextraction

conditions (such as pH of sample, salt concentration etc.) or by sorbent modification.

**Compliance with ethical standards** The author(s) declare that they have no competing interests.

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