



Performance of metal-organic framework as an excellent sorbent for highly efficient and sensitive trace determination of anthracene in water and food samples

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Received: 15 December 2019 / Accepted: 22 April 2020 / Published online: 2 May 2020
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Abstract

Polycyclic aromatic hydrocarbons are a class of highly toxic and unremitting organic pollutants that are widely distributed in the natural environment. In this work, a metal-organic framework (MOF) designated as HKUST-1 [Cu₃(BTC)₂] was synthesized, characterized, and applied as a solid-phase extraction sorbent for the determination of a trace polycyclic aromatic hydrocarbon, anthracene (Ant) as model compound, in various real samples by spectrofluorimetry. The synthesized MOF exhibited large surface areas and high extraction ability, making it excellent candidate as sorbent for enrichment of trace anthracene. The effects of influential parameters on the performance of the dispersive micro-solid-phase extraction (D μ -SPE) process, such as the initial anthracene concentration, pH, sorbent dosage, and shaking time, were investigated and optimized by the experiment design method. Under the optimized experimental conditions, good linearity in the range of 3–85 ng mL⁻¹ with correlation coefficient 0.997 and good sensitivity with low detection limit 0.5 ng mL⁻¹ for Ant was achieved. The method has been validated in the analysis of real tap water, soft drink, and vegetable juice samples with recoveries in the range of 86.33–103.00% and relative standard deviations in the range of 1.94–3.77%. The as-prepared HKUST-1 was used for at least four times without any obvious decline of extraction capability. The results of this study show the great potential of MOFs as sorbents in D μ -SPE procedures for the separation and determination of trace Ant in complicated matrices.

Keywords Anthracene · Metal-organic frameworks · Multivariate optimization · Polycyclic aromatic hydrocarbons · Vegetable juice samples

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are basically produced by incomplete combustion of organic matter, and some of these compounds have high carcinogenicity and mutagenicity (Kim et al. 2013; Van der Wat and Forbes 2019). Anthracene (Ant) has been listed as one of the priority environmental pollutants by the US Environmental Protection Agency (EPA) (Wang et al. 2015). Owing to the conjugate system in the molecule structure, Ant is stable in the environment (Marce and Borrull 2000). Due to low concentration and

wide distribution of PAHs in all parts of the environment (soil, water, and atmosphere), the enrichment procedure is usually required prior determination.

Dispersion of micro or nanosorbents in sample solution is a miniaturized extraction method known as dispersive micro-solid-phase extraction (D μ -SPE) (Chisvert et al. 2019; Karimi-Maleh et al. 2020). Dispersion phenomenon enables the sorbent to interact quickly and uniformly with all the target analytes which leads to reduction of the extraction time and enhancement of the accuracy of method (Khezeli and Daneshfar 2017; Khani et al. 2019). In order to obtain a sensitive and selective determination using D μ -SPE, nature and physicochemical properties of the selected sorbent are very momentous. Therefore, it is crucial to develop a high-capacity adsorbent which can effectively and rapidly use for the extraction and determination trace levels of target compounds in various matrices. Diverse adsorbents such as activated carbon, modified silica gel, and nanoparticles (NPs) have been used in solid-phase extraction (Pérez-López and Merkoçi 2012; Azzouz et al. 2018).

Responsible editor: Tito Roberto Cadaval Jr

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Metal-organic frameworks (MOFs), which are composed of metal-oxo clusters and organic ligands, are emerging class of hybrid porous materials that have large interparticle spaces adequate for loading guest molecules (Yaghi et al. 2019). Their facile preparation in combination with unrivaled physical and structural features such as high surface areas, high thermal stability, and easy tunable composition in comparison with common porous materials (e.g., zeolites and porous carbons) makes them ideal for separation and the selective sorption of various organic compounds (Hashemi et al. 2017; Hu et al. 2019; Yue et al. 2016; Zhao et al. 2019). Among different types of MOFs, the copper-based MOFs [Cu₃(BTC)₂] (known as HKUST-1 or MOF-199) (BTC = 1,3,5-benzenetricarboxylate) with available nano cavities have been widely studied (Prestipino et al. 2006; Cai et al. 2014).

In the present work, a metal-organic framework, HKUST-1, [Cu₃(BTC)₂], was synthesized and explored as an excellent sorbent for D μ -SPE of anthracene as model compound from the different real samples (tap water, soft drink and vegetable juice) using spectrofluorimetry at trace levels. Characterization of the synthesized sorbent was evaluated by Fourier transform infrared spectroscopy (FT-IR), Brunauer-Emmett-and Teller (BET) nitrogen adsorption isotherm, scanning electron microscopy (SEM), and X-ray diffraction (XRD). Response surface methodology with central composite design (CCD) has been used to optimize the influence of important variables on the extraction recovery of Ant.

Experimental

Materials

Anthracene and benzene-1, 3, 5-tricarboxylic acid (trimesic acid) were of analytical grades and purchased from Merck (Darmstadt, Germany, <http://www.merck.de>). The different eluents including acetonitrile, methanol, ethanol, and acetic acid were of analytical grades and obtained from Aldrich (Chemical Co., Milwaukee, WI, USA, www.sigmaaldrich.com). All aqueous solutions were prepared in double-distilled deionized water (Milli-Q system, Millipore, USA). A stock solution of the anthracene (100 mg L⁻¹) was prepared in methanol and stored at 4 °C. Working standard solutions were prepared by diluting and mixing the individual stock solutions. Laboratory glassware was kept overnight in a 10% v/v HNO₃ solution and then rinsed with double-distilled deionized water.

Apparatus and software

A Shimadzu RF-5301PC spectrofluorometer (Shimadzu, Japan) equipped with quartz cell and 5 nm the excitation and emission slit widths was applied for recording of the

fluorescence spectra. The ultrasonic bath (James Ultrasonic system, 37 KHz and 160 W, England) and centrifuge (Hettich ZENTRIFUGEN ROTOFIX 32 A, Kirchleugern, Germany) were used for the synthesis and proposed microextraction processes. For the pH adjustment, a digital pH meter (HANNA instruments HI 2211 pH/ORP Meter) was used.

The statistical optimization of the experiments was accomplished using the Design-Expert Software Version 10.0.0 (Statistical Graphics, Rockville, USA).

Synthesis of MOF

According to the previously reported procedure, Cu₃(BTC)₂ designated as HKUST-1 was synthesized (Chui et al. 1999). Typically, a suspension of H₃BTC (2.52 g, 12 mmol) in 120 mL deionized water (sonicated for 5 min) was added rapidly into a solution of Cu(OAc)₂·H₂O (1.2 g, 6 mmol) in 120 mL double-distilled deionized water with strong stirring (1200 rpm) for 24 h at room temperature. The product was collected with centrifugation (6000 rpm, 12 min) for three times and dried at 100 °C under vacuum overnight.

D μ -SPE procedures by HKUST-1 as adsorbent

In a polypropylene conical centrifuge tube, 20 mg of as-prepared HKUST-1 as adsorbent to 25 mL of a standard solution containing 60 ng mL⁻¹ of the Ant at pH 6.6 was added. To simplify adsorption of the Ant on the surface of HKUST-1, the suspension was shaken for 22 min. After a 10-min centrifugation at 5000 rpm, the dispersed MOF with adsorbed target compound was sedimented at the bottom of the conical centrifuge tube. Then, the preconcentrated target analyte was desorbed from the HKUST-1 by addition of 1.5 mL methanol during 5 min sonication. Finally, the fluorescence intensity of Ant was measured at 420 nm with the excitation wavelength set at 340 nm.

Sample collection and pretreatment

The efficiency of the proposed method was evaluated by separation/preconcentration and determination of Ant in three types of real samples including tap water, soft drink ready to consume, and vegetable juice samples. The soft drink (Fanta brand) and carrot and celery samples were purchased from a local supermarket in Birjand (South Khorasan Province, Iran). After purchase, the vegetation samples were bagged and kept refrigerated at 4 °C, till analyzed. The selected real samples were collected and prepared according to the following procedures.

1. Water samples

Tap water sample was collected from our laboratory (University of Birjand, Birjand, Iran) after flowing for 5 min and used without prior treatment.

2. Soft drink and vegetable juice samples

Ten milliliters of a soft drink (Fanta brand) was diluted with double-distilled deionized water to the mark in a 50-mL measuring flask. Samples of vegetable juice (Carrot and Celery) were obtained by crushing, cleaning, and peeling carrot and celery. The prepared carrot and celery juice samples were filtered through 0.45 μm Whatman filter paper and poured into clean sealed bottles. Then, carrot and celery juice samples were diluted at 1: 20 and 1:10 ratio with double-distilled deionized water before the extraction, respectively. All the real samples were extracted and analyzed within 24 h.

Experimental design

Multivariate optimization techniques through fast and effective pathway widely are applied in optimization of procedures (Khani et al. 2016). In the present work, a five-level central composite design (CCD) as one of the most applicatory simultaneous optimization methods (Rosales et al. 2012; Khani et al. 2018) using Design-Expert software (version 10.0) was employed to maximize the percentage extraction recovery (ER %) of Ant. Four input parameters such as initial concentration of Ant (A), pH (B), amount of HKUST-1 (C), and shaking time (adsorption time) (D) in a randomized manner are used to study the effects on the ER% of Ant (see Table 1).

Results and discussion

Structural characterization of the prepared sorbent

FT-IR spectrum of HKUST-1 MOF (Fig. 1a) discloses a very broad peak at 3100–3600 cm⁻¹ that indicated the presence of loosely bound water molecules in Cu-BTC (Bagheri et al. 2012; Nakamoto 2006). At 1384, 1405 cm⁻¹, and 1508–1623 cm⁻¹, the symmetric and asymmetric stretching of the carboxylate groups in H₃BTC is detected, respectively. The

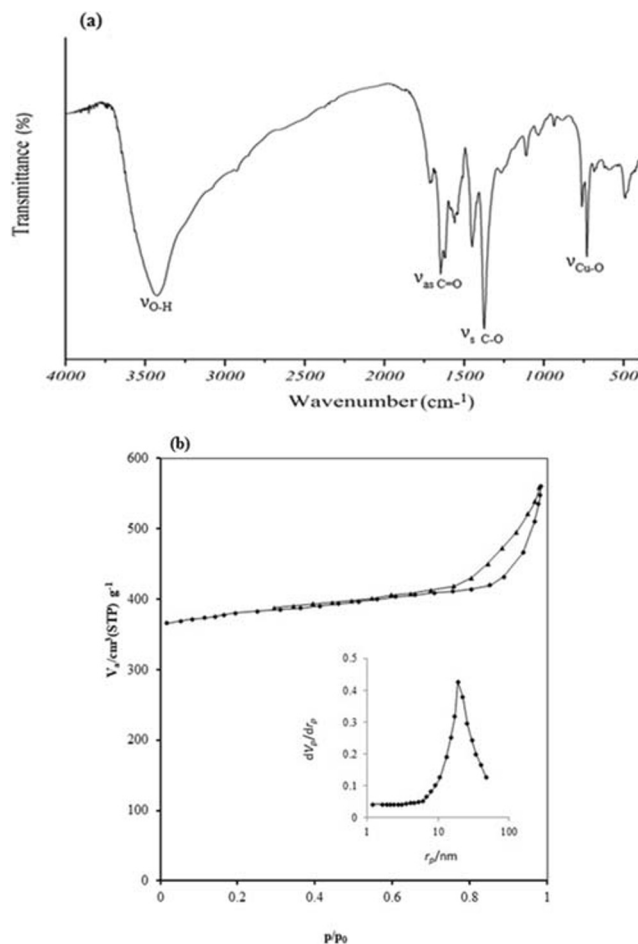


Fig. 1 a FT-IR spectrum. b Nitrogen adsorption–desorption isotherm and BJH pore size distribution of as-synthesized HKUST-1

several bands in the region of 1300–600 cm⁻¹ are devoted to the out-of-plane vibrations of H₃BTC. The characteristic vibration at 730 cm⁻¹ might be attributed to Cu–O stretching vibration, in which the oxygen atom was coordinated with Cu.

The N₂ adsorption–desorption isotherms of Cu-BTC and the corresponding pore size distributions at 77 K are reported in Fig. 1b. The as-synthesized MOF sample showed type-IV adsorption–desorption isotherm, obviously, demonstrating its typical mesoporous network. In addition, the N₂ adsorption–desorption isotherms of HKUST-1 revealed that BET surface area of HKUST-1 was found to be 1168.4 m² g⁻¹ and the pore

Table 1 Independent variables and their levels in the CCD for determination of Ant

Independent variables	Symbols	Unit	Range and levels				
			-α	-1	0	+1	+α
Conc. Ant	A	mg L ⁻¹	0.02	0.04	0.06	0.08	0.1
pH	B	-	2	4	6	8	10
MOF dosage	C	mg	5	10	15	20	25
Shaking time	D	min	10	15	20	25	30

volume was $0.55 \text{ cm}^3 \text{ g}^{-1}$, which were similar to the reported values in the literature (Rocio-Bautista et al. 2015; Chui et al. 1999).

The morphology of the synthesized HKUST-1 can be observed by scanning electron microscopy (SEM) image that is presented in Fig. 2. The synthesized HKUST-1 is octahedral with clear edges and has an average size of 15–20 μm .

PXRD patterns of the prepared sample and simulated of HKUST-1 MOF (Chui et al. 1999) are shown in Fig. 3. It is evident that the discrete and sharp peaks in the diffraction pattern of as-synthesized sample match well with the simulated ones, indicating that the attained sample is pure phase and presented the well-defined crystallinity of the HKUST-1.

Effect of sample volume

To optimize the sample volume in the D μ -SPE process, various volumes (10, 15, 25, and 50 mL) of sample solutions with 60 ng of Ant under the same extraction conditions were studied. The results showed that the highest extraction recovery was obtained at the sample volume of 25 mL (Fig. 4). In the sample volumes higher than 25 mL, probably due to the insufficiency of interaction between the HKUST-1 and the larger sample solution, the ER% decreased. Accordingly, the volume of 25 mL was chosen as the optimal sample volume for further experiments.

Selection of desorption conditions

For the choice of an appropriate type of eluent, different eluents including acetonitrile, methanol, ethanol, acetic acid 0.1 M, and acetic acid 0.2 M for desorption of Ant from the HKUST-1 were selected and investigated. Under the same extraction and elution conditions, the obtained results showed that methanol has better desorption ability compared with other eluents. The volume of eluent (0.5, 1, 1.5, 2, and 2.5 mL) was also optimized, and the results exhibited that effective

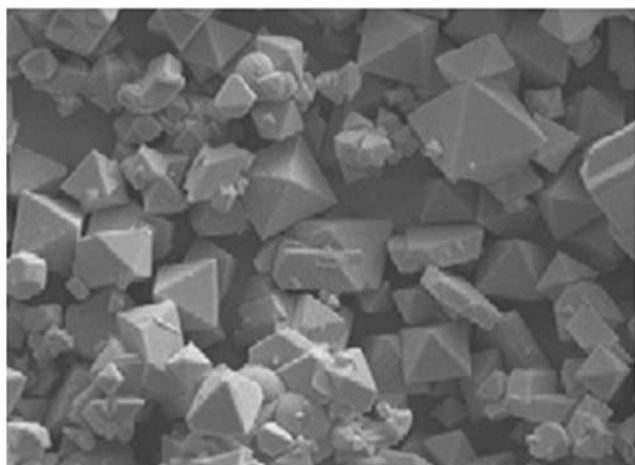


Fig. 2 SEM image of as-synthesized HKUST-1 MOF s, scale bar: 1 μm

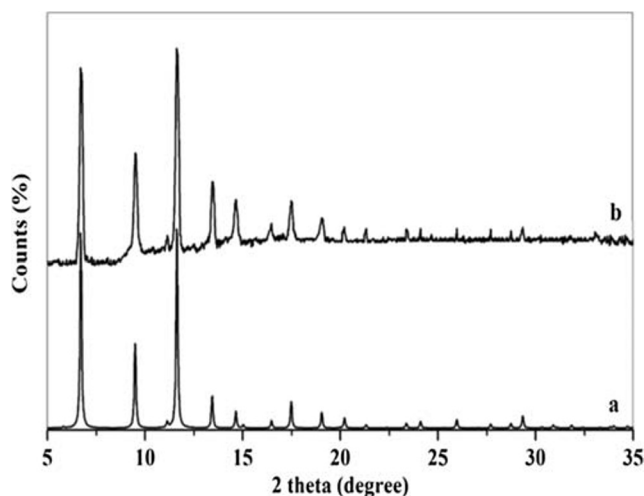


Fig. 3 Simulated PXRD pattern of HKUST-1. b PXRD pattern of as-synthesized MOF

elution was achieved with 1.5 mL of methanol as eluent, and the recoveries of target compound were in the range of 88.0–96%. Therefore, 1.5 mL of methanol was chosen in the subsequent analysis.

ANOVA and development of regression model

Analysis of variance (ANOVA) as the most powerful numerical method based on the F-test and considering p value at 95% confidence level was used for model validation (Chagas et al. 2019). The best correlation between extraction recovery and input parameters was selected in following equation:

$$\text{ER}\% = 93.30 + 1.40*A + 5.98*B + 3.01*C + 1.46*D + 2.30*BC - 5.47*A^2 - 15.52*B^2 - 1.71*C^2 \quad (1)$$

According to the ANOVA results (Table 2), the high significance of the model was confirmed by a very high F-value ($F_{\text{model}} = 115.46$) and a very low p value ($P_{\text{model}} < 0.0001$). The F-value and p value (p values < 0.05) suggested that A, B, C, D, A^2 , B^2 , C^2 , and BC are the significant terms. p value

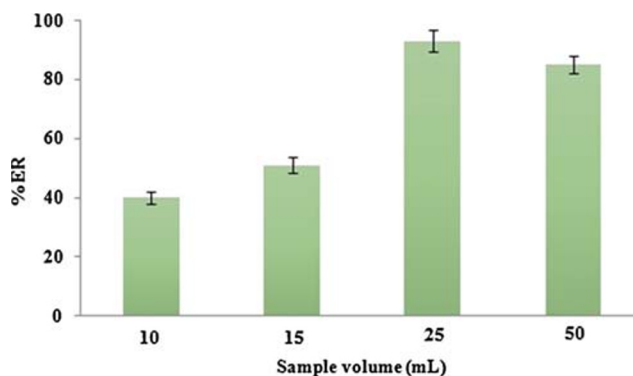


Fig. 4 Effect of initial sample volume on the extraction recovery of Ant

0.1927 for lack of fit as a non-significant term indicates the desirability and appropriateness of the model equation to predict extraction recovery. The high value of correlation coefficient ($R^2 = 0.992$) indicated a very good correlation and accuracy of the proposed model (Yasini et al. 2012). The predicted R^2 parameter value was obtained 0.940, which is closely matched with the adjusted R^2 value (0.984) of parameter.

Assessment of diagnostic, response surface, and contour plots

The normal probability plot (NPP) (Fig. 5a) shows a normal distribution of the residuals for response, which is suitable and excellent (Khani et al. 2018). Figure 5 b illustrates the predicted values versus the actual values, stating that the high validity of the proposed model.

Figure 6 shows response surface and contour plots (Khani et al. 2019) of understudied variables on ER % of Ant. Effect of initial Ant concentration ($\mu\text{g mL}^{-1}$) and pH on %ER of Ant (Fig. 6a) discloses that the extraction efficiency decreases with increases in initial Ant concentration. At lower Ant concentrations (lower than $0.07 \mu\text{g mL}^{-1}$), due to the accessibility of high surface area of unoccupied sites of HKUST-1, better diffusivity of Ant to HKUST-1 occurs. In higher concentrations than $0.07 \mu\text{g mL}^{-1}$, the saturation of available sites of adsorbent takes place and the extraction recovery decreases. The pH influence on the extraction efficiency of the Ant was

inspected in the range from 2.0 to 10.0. With regard to the plots, satisfactory extraction recoveries of Ant were achieved in the pH range of 6–7.5.

Figure 6 b shows the interaction between the effect of shaking time and pH on the ER% of Ant. As can be seen, the ER% of Ant showed an enhancement trend with the rise of shaking time up to 22 min, and then changed slightly. This could be due to the very high number of unoccupied surface and reactive sites in HKUST-1 at the initial stage of adsorption. Subsequently, with saturation of reactive sites during the $D\mu$ -SPE process, the ER % slightly decreases.

The effect of HKUST-1 dosage on the extraction of Ant (Fig. 6c) demonstrated that by increasing the mass of HKUST-1 due to more surface area and accessibility of high adsorption sites, the ER% of target compound increased. Further increase in the HKUST-1 dosage (more than 20 mg) has not any considerable change in the adsorption.

Optimal conditions for $D\mu$ -SPE of Ant

In order to determine the optimal conditions for the studied parameters, the desirability function (DF) approach was used. Maximum ER% as the desirability function and all studied parameters were considered in the range of the study. The optimal conditions for the initial Ant concentration, pH, amount of HKUST-1, and shaking time were 60 ng mL^{-1} , 6.6, 20 mg, and 22 min, respectively, with the desirability of

Table 2 The ANOVA results of the response surface quadratic model for determination of Ant

Source	Sum of squares	DF ^a	Mean squares	F-Value	p Value	
Model	8360.37	14	597.17	115.17	<0.0001	Significant
A	42.04	1	42.04	8.13	0.0146	
B	767.80	1	767.80	148.45	<0.0001	
C	193.88	1	193.88	37.49	<0.0001	
D	45.61	1	45.61	8.82	0.0117	
AB	0.31	1	0.31	0.059	0.8121	
AC	13.58	1	13.58	2.62	0.1312	
AD	5.74	1	5.74	1.11	0.3130	
BC	71.81	1	71.81	13.89	0.0029	
BD	12.91	1	12.91	2.50	0.1402	
CD	8.69	1	8.69	1.68	0.2193	
A ²	814.14	1	814.14	157.41	<0.0001	
B ²	6552.08	1	6552.08	1266.83	<0.0001	
C ²	79.18	1	79.18	15.31	0.0021	
D ²	3.03	1	3.03	0.59	0.4589	
Residual	62.06	12	5.17			Not significant
Lack of Fit	55.99	55.99	6.22	3.07	0.1927	
Pure Error	6.07	3	2.02			
Cor. Total ^b	8464.50	28				

^a Degrees of freedom

^b Totals of all information corrected for the mean

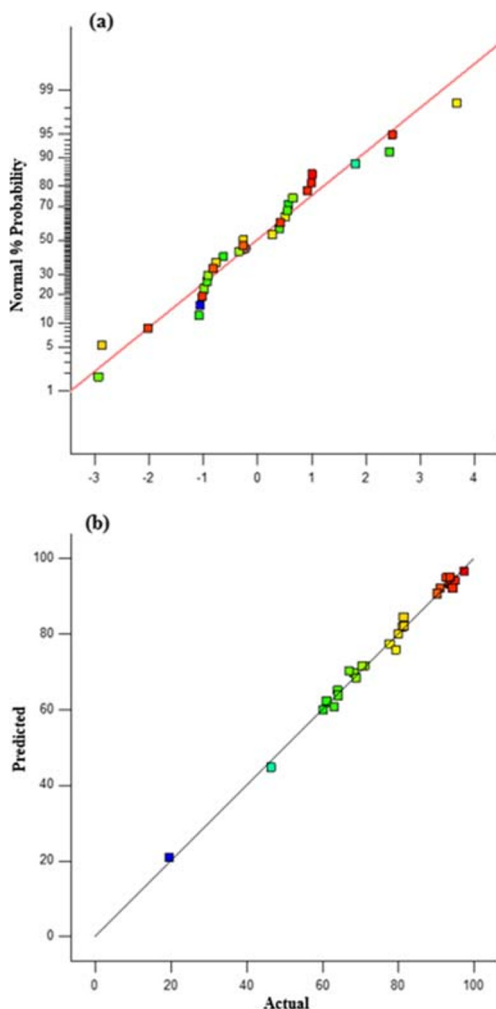


Fig. 5 **a** Normal probability plot for the residuals. **b** The actual data vs. the predicted data of %ER of Ant

0.988. The performance of five replicates at the abovementioned optimum conditions showed a very good compliance with predicted results.

Reusability of HKUST-1

Regeneration of the adsorbents for various adsorption/desorption cycles to reduce the extraction time and cost was required. The adsorbent was regenerated with 1.5 mL of methanol and then by washing with 5 mL water before the each D μ -SPE application. As can be seen in Fig. 7, after four consecutive extraction operations, no clear changes were observed in the extraction recovery. According to the obtained results, the proposed sorbent is stable during the D μ -SPE procedure.

Study of interference substances

The effect of the potentially interfering substances during the D μ -SPE of 0.05 $\mu\text{g mL}^{-1}$ Ant under optimal experimental

conditions was investigated. From the tolerance results in Table 3, it can be seen that high levels of the ions have no impact on the ER% and determination of Ant. Three compounds, phenol, P-nitrophenol, and naphthalene, can be tolerated up to 50–100-fold. The results imply that the synthesized HKUST-1 sorbent is selective to Ant with regard to generally found interferences in the water, soft drink, and vegetable juice samples.

Evaluation of analytical performance

To assess the performance of the proposed method, different analytical quality parameters under the optimal experimental conditions were evaluated. Good linearity was obtained for the target analyte in the range of 3–85 ng mL^{-1} with $R^2 = 0.997$ (Fig. 8). The limits of detection (LOD) and quantification (LOQ), based on 3 and 10 S_b/m (S_b is the standard deviation of the blank and m is the slope of the calibration graph), were calculated and obtained of 0.5 and 1.65 ng mL^{-1} , respectively. The precision of the method, discerned as the relative standard deviation (RSD, %) for 50 ng mL^{-1} of Ant, was found to be 1.2% ($n = 5$). These results asserted that the HKUST-1 as D μ -SPE sorbent was quite efficient and reproducible.

Application to analysis of Ant in tap water, soft drink, and vegetable juice samples

To evaluate the performance of the developed approach, the HKUST-1-based D μ -SPE method was applied for the extraction and determination of Ant in various real samples, such as tap water, soft drink, and vegetable juice samples. To further evaluate the matrix effect, the mentioned real samples were spiked with standard solutions at three different concentrations of 20, 30, and 50 ng mL^{-1} . As presented in Table 4, the mean recoveries of Ant were in the range of 86.33–103% for the spiked real samples. Besides, the relative standard deviations (RSDs) of three experiments were all below 4%. The obtained results exhibited the good availability and high precision of the D μ -SPE method based on the HKUST-1 MOF as adsorbent in the analysis of real samples with different matrices.

Comparison of the current study with previously reported methods

Table 5 displays a comparison between the obtained analytical results of the proposed method and some of the reported methods for the determination of Ant. As reported in Table 5, the determination of PAHs has mainly been focused on combination of separation methods such as high-performance liquid chromatography (HPLC) and gas chromatography (GC) with sample pre-treatment techniques

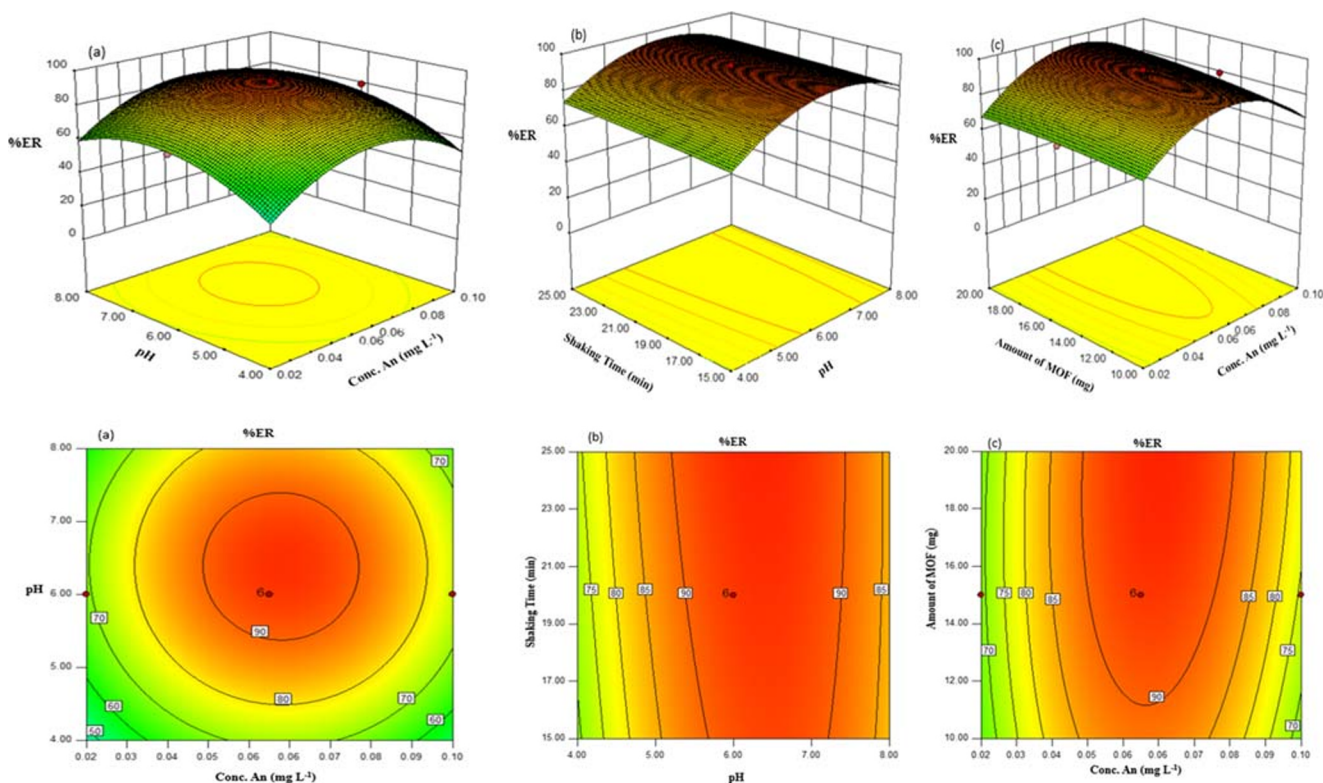


Fig. 6 Response surface and contour plots for Ant extraction recovery. **a** pH and concentration of Ant. **b** pH and shaking time. **c** Amount of MOF and concentration of Ant

including SPE and solid-phase microextraction (SPME). Some disadvantages arise from mentioned instrumental methods, such as usage of toxic solvents and expensive equipments, the need of tedious sample pre-treatments for complex matrices, and the resulting waste products. In the extraction of PAHs by SPE using reversed-phase, depending on the solvent used, adsorption problems related to PAH solubility can be found (e.g., adsorption onto the glassware walls) (Plaza-Bolaños et al. 2010). Moreover, one of the main problems when using SPME is matrix effect, causing a decrease in the fiber efficiency. Generally, the SPME methodologies are limited with respect to precision. This is one of its drawbacks, the

lack of reproducibility, together with a short lifetime of the fibers and possible carry-over problems (Plaza-Bolaños et al. 2010). Furthermore, the long adsorption equilibrium time and comparatively high cost significantly restrict the extensive use of SPME in routine analysis. In addition to the reported methods in Table 5, Bogusz et al. (Bogusz et al. 2004) carried out a comparison between the performance of SPE and matrix solid-phase dispersion (MSPD) for the extraction of PAHs from olive oil. The main advantage of MSPD is the low amount of solvent needed. Nevertheless, reproducibility problems are often observed, with medium-high RSD values. Moreover, MSPD provided lower recoveries and worse repeatability than the SPE procedure used. PAHs have been also

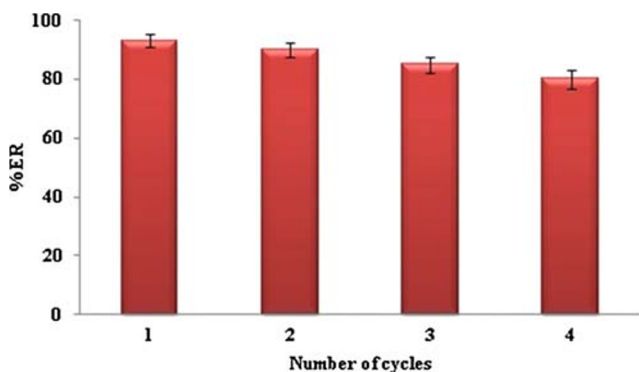


Fig. 7 Effect of number of recoveries of HKUST-1 sorbent on the extraction recovery of Ant

Table 3 The effect of different substances on the extraction recovery of Ant

Foreign substances	Tolerance ratio
Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺ , Cl ⁻	4000 (3.8) ^a
Co ²⁺ , Cr ³⁺ , Cu ²⁺ , Zn ²⁺	2000 (2.4)
Ni ²⁺ , Cd ²⁺	1000 (3.3)
SO ₄ ²⁻ , CH ₃ COO ⁻	1500 (2.7)
Phenol and P-nitro phenol	50 (4.2)
Naphthalene	30 (3.6)

^a The relative standard deviation (*n* = 3)

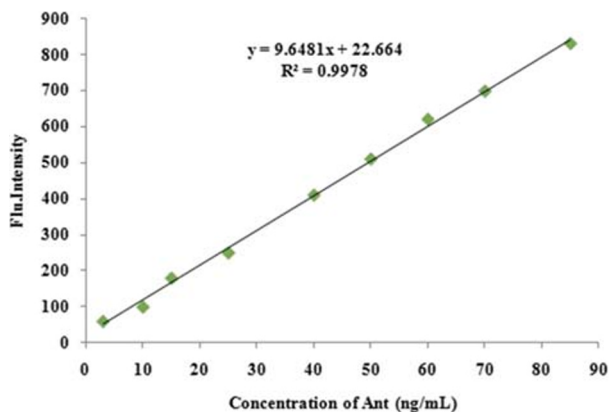


Fig. 8 Calibration curve of Ant at optimal condition

determined by head space (HS) and head space solid-phase microextraction (HS-SPME) (Arrebola et al. 2006; Vichi et al. 2005). The use of HS-SPME technique reduces sample handling and minimizes solvent consumption, but some drawbacks have been reported, such as overloading problems due to insufficient coating film of the fibers (Viñas et al. 2007). Dispersive micro-solid-phase extraction (D μ -SPE) has gained special attention in the sample preparation process due to its simplicity, speed, and efficiency. Dispersion of the sorbent enhances the extraction kinetics and makes possible the utilization of all the sorbent capacity of a given material (Chisvert et al. 2019). Accordingly, the D- μ -SPE based HKUST-1 as sorbent combined with fluorescence detection has lower RSD, wide linear dynamic range, and comparable limit of detection compared with the majority of the other approaches. Also, the proposed method shows the advantages of easiness and low toxic organic solvent consumption combined with the inherently high sensitivity and selectivity characteristics of fluorescence detection without complicated and time-consuming

Table 4 Results for the determination of Ant in the tap water, soft drink, carrot juice, and celery juice samples (n = 3)

Matrix	Added (ng mL ⁻¹)	Found (ng mL ⁻¹)	%RRE ^b
Tap water (Birgand city)	0	Not detected	–
	20	20.4 ± 0.4 ^a	102.00
Soft drink ^c	0	Not detected	–
	50	46.2 ± 1.0	92.40
Carrot juice	0	5.3 ± 0.2	–
	30	32.0 ± 0.8	89.00
Celery juice	0	3.7 ± 0.1	–
	30	29.6 ± 1.0	86.33

^a The standard deviation (n = 3)

^b Relative recovery extraction

^c Fanta soft drink

Table 5 The comparison between the suggested method based on MOF and some reported methods for determination of Ant

Method	Detection	LDR (ng mL ⁻¹)	LOD (ng mL ⁻¹)	RSD (%)	Sample	Refs.
SPE	RP-HPLC-UV ^a	0.34–14.11	20	6	Caspian Sea water	Habibi and Hadj Mohammadi (2008)
MSPF ^b	Spectrophotometry	0.8–20	0.21	4.1	Water	Ghasemi and Zolfonoun (2013)
SPME ^c	GC-FID ^d	2–400	0.20	5	Rian water	Liu et al. (2018)
SPME	GC-MS ^e	0.01–10	0.59	8.4	Environmental water	Sun et al. (2019)
SPE	Spectrofluorometry	20–1000	10	4	Cellulose tissue	Dyachuk et al. (2009)
D-SPE ^f	GC-MS	6.55–7.56	0.22	–	Coffee	Sadowska-Rociek et al. (2015)
SPE	HPLC	0–100	46	–	River water	Moja et al. (2013)
SPE	HPLC	–	125	11	Wastewater	Oleszczuk and Baran (2004)
D μ -SPE	Spectrofluorometry	3–85	0.50	1.2	Tap water, Soft drink and Vegetables juice	This work

^a Reverse phase-high performance liquid chromatography-ultraviolet

^b Magnetic solid-phase extraction

^c Solid-phase microextraction

^d Gas chromatography-flame ionization detection

^e Gas chromatography-mass spectrometry

^f Dispersive solid-phase extraction

derivatization procedure. In addition, in the present study, the chosen matrices (tap water, soft drink and vegetables juice samples) are more complex than the other reported works in Table 5 (mainly water samples). In fact, separation and determination of target compounds from various and complex matrices is a main advantage for a proposed method in analytical works and indicates the robust performance of the method. Therefore, the present method is efficient, sensitive, and no need for any expensive instrument, which are of a key interest for routine target compounds analysis.

Concluding remarks

In this work, HKUST-1 MOF was synthesized, characterized, and explored as an excellent adsorbent for dispersive micro-solid-phase extraction (D μ -SPE) of trace Ant. D μ -SPE due to speed, simplicity, and efficiency has achieved special attention in the sample preparation process. The dispersion process in D μ -SPE helps that the kinetics of sorption, elution, and subsequently the efficiency of the extraction procedure increases. Central composite design coupled with desirability function method was applied to investigate and optimize the influential parameters. Owing to the large surface area, strong π - π stacking interaction between MOFs and PAHs and the inherently high sensitivity and selectivity characteristics of fluorescence detection, the proposed method showed wide linearity and good sensitivity and accuracy. Additionally, D μ -SPE-based HKUST-1 as sorbent combined with fluorescence detection was successfully utilized to analyze Ant in real tap water, soft drink, and vegetable juice samples with satisfactory extraction recovery (%ER > 86%) and precision (%RSDs < 4%). Thus, it is expected that the suggested method has a great potential for the rapid and efficient separation/preconcentration and determination of trace target compounds from various real samples with complicated matrices in the similar way.

Funding information The financial support from the University of Birjand.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Ethical approval This article does not contain any studies with human participants or animals performed by any of the authors.

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