



Research article

Evaluation of metal-organic framework NH₂-MIL-101(Fe) as an efficient sorbent for dispersive micro-solid phase extraction of phenolic pollutants in environmental water samples



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ABSTRACT

This work proposes an application of amine-functionalized metal-organic framework (NH₂-MIL-101(Fe)) as sorbent for dispersive micro-solid phase extraction (D- μ SPE) of ten priority phenolic pollutants. The sorbent was simply synthesized under facile condition. The entire D- μ SPE process was optimized by studying the effect of experimental parameters affecting the extraction recovery of the target analytes. The final extract was analyzed using high performance liquid chromatography with photodiode array detector. Under the optimum condition, the proposed procedure can be applied for wide linear calibration ranges between 1.25–5000 $\mu\text{g L}^{-1}$ with the correlation coefficients of greater than 0.9900. The limits of detection (LODs) and limits of quantitation (LOQs) were in the ranges of 0.4–9.5 $\mu\text{g L}^{-1}$ and 1.25–30 $\mu\text{g L}^{-1}$, respectively. The precision evaluated in terms of the relative standard deviations (RSDs) of the intra- and inter-day determinations of the phenol compounds at their LOQ concentrations were below 13.9% and 12.2%, respectively. High enrichment factors up to 120 were reached. The developed method has been successfully applied to determine phenol residues in environmental water samples. The satisfactory recoveries obtained by spiking phenol standards at two different concentrations (near LOQs and 5 times as high as LOQs) ranged from 68.4–114.4%. The results demonstrate that the NH₂-MIL-101(Fe) material is promising sorbent in the D- μ SPE of phenolic pollutants.

1. Introduction

Metal-organic frameworks (MOFs) are inorganic-organic hybrid microporous crystalline materials constituted by metal clusters connected by organic linkers. Due to their fascinating diverse structures with tailorable chemistry, large surface areas, tunable pore sizes, good thermal stability and chemical resistance, MOFs have been demonstrated for applications in various fields such as gas storage [1, 2], catalysis [3, 4], chemical sensing [5], adsorption [6, 7], and separation [3, 8]. A large number of reports have also shown that MOFs possess great potential in a field of analytical chemistry [8, 9, 10, 11, 12, 13]. UiO-66, a cubic rigid 3D porous MOF-self-assembled from zirconium clusters Zr₆O₄(OH)₄ and terephthalate ligands, was coated on stainless steel fiber for solid-phase microextraction (SPME) of polar phenols in water samples [14]. An NH₂-MIL-53(Al) incorporated poly(styrene-divinylbenzene-methacrylic acid) monolith was efficiently applied to the in-tube solid-phase microextraction for determination of trace estrogens in human urine samples

[15]. The prepared monolith showed good reproducibility up to 100 cycles of extraction. For application as sorbent materials in solid-phase extraction (SPE), MIL-101(Cr) and MIL-101(Cr) intercalated by poly-aniline composite and doped with silica nanoparticles were synthesized and applied for determination of sulphonamides and thymol and carvacrol, respectively [16, 17].

Nowadays, SPE-based miniaturized technique, dispersive micro-solid phase extraction (D- μ SPE) is acquiring a lot of attention due to the impressive decrease in the amounts of sorbents required. D- μ SPE is based on direct dispersion of the small amount of sorbent in a sample solution containing target analytes, extraction by sorption, separation of the sorbent with retained analytes from the solution, and following by solvent elution of the analytes. In applications involving MOFs as sorbents, the partitioning of various analytes to different MOFs was evaluated. To find a versatile MOF able to extract contaminants with different chemical and physical properties and to establish the relationships between MOF structure-analyte nature, Rocío-Bautista et al. studied the five types of

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MOFs, including HKUST-1, MOF-5(Zn), MIL-53(Al), UiO-64 and MOF-74(Zn), for determination of six emerging pollutants of different nature [18]. The pore size, the presence of unsaturated metal sites, and the nature of metal have a major influence in their extraction efficiencies. In addition, UiO-66, UiO66-NH₂, UiO-66-NO₂ and MIL-53(Al) were studied for determination of different aqueous organic pollutants in environmental waters [19]. The presence of functional groups in the ligands of UiO-66 influence the total efficiency of the method, particularly due to the polar character given to the organic linkers. Among the MOF-type materials used in many sample preparation applications, MILs have been utilized as promising candidates due to their superior characteristics when compared with other MOFs, including high surface-to-volume ratio, porosity, and lower costs [17]. A variety of MILs have been prepared and applied in development of SPE methods, such as amino-functionalized MIL-53(Al) for preconcentration of phenolic pollutants [20, 21], MIL-101(Cr) for phthalate esters [22], MIL-101(Cr)@GO for sulfonamides [23], Fe₃O₄@MIL-100 for polychlorinated biphenyls [24], and MIL-101 for pyrazole/pyrrole pesticides [25].

Phenol and its derivatives i.e. chlorophenols, nitrophenols and methylphenols are one of the most toxic water pollutants, which exist in the environment due to the activity of the chemical, pharmaceutical, and petrochemical industries [26]. Owing to their high toxicity even at low concentrations, low degradable and prevalent presence in environment, the United States Environmental Protection Agency (US EPA) and the European Union (EU) have classified them as priority pollutants in aquatic environment. Therefore, determination of these compounds is of great importance for awareness and prevention of related human diseases.

Quantification of phenol and its derivatives are mainly based on selective chromatographic techniques, i.e. gas chromatography (GC) [14, 27] and high performance liquid chromatography (HPLC) [20, 21, 28, 29]. However, direct determination is difficult to achieve due to the complex matrices and their presence at low concentration levels. Thus, sample pretreatment is required prior to instrumental analysis. For this reason, different extraction methods have been developed. In the present work, we aimed to explore NH₂-MIL-101(Fe) as sorbent for development of D- μ SPE for ten priority phenolic pollutants, including phenol (Ph), 4-nitrophenol (4NP), 2-chlorophenol (2CP), 2,4-dinitrophenol (24DNP), 2-nitrophenol (2NP), 2,4-dimethylphenol (24DMP), 4-chloro-3-methylphenol (4C3MP), 2,4-dichlorophenol (24DCP), 2-methyl-4,6-dinitrophenol (2M46DNP), and 2,4,6-trichlorophenol (246TCP). Extraction process was accelerated using vortex agitation. The NH₂-MIL-101(Fe) was simply synthesized under facile condition when compared with other types of MOF-based materials. Experimental parameters affected the extraction efficiency of the developed procedure were carefully optimized. The method was validated and successfully applied for determination of phenol residues in surface water samples.

2. Experimental

2.1. Chemicals

Analytical phenol standards with a purity of $\geq 99\%$ were used in this work. 24DNP, 4C3MP, 2M46DNP, 246TCP and 24DMP were supplied by Sigma-Aldrich (Germany). Ph was obtained from Sigma-Aldrich (USA). 4NP and 24DCP were purchased from Sigma-Aldrich (India). 2NP was supplied by Fluka (China). 2CP was supplied by Sigma-Aldrich (China). Stock standard solutions of phenols at concentration of 1000 $\mu\text{g mL}^{-1}$ were prepared using methanol as the solvent. Working solutions were prepared daily by dilution with water. Deionized water (18.2 M Ω -cm) obtained by a RiOs Type I Simplicity 185 water purification system (Millipore, USA) was used in all experiments. 2-Aminoterephthalic acid (99%, Sigma-Aldrich, USA), N,N-dimethylformamide (DMF, $\geq 99\%$, Merck, Germany), and ferric chloride anhydrous ($\geq 98\%$, Riedel-de Haën, Germany) were used for synthesis of amine-functionalized MOF sorbent. Acetonitrile (isocratic grade, Merck, China), methanol (gradient grade,

Merck, Germany), ethanol (AR grade, Merck, Germany), acetone (AR grade, Qręc, New Zealand) and glacial acetic acid (AR grade, Carlo Erba, Italy) were used for HPLC separation and DSPE procedure.

2.2. Apparatus

The HPLC system (Waters, USA) consisted of an in-line degasser, a 600E quaternary pump, and a Waters 2996 photodiode array (PDA) detector. Empower software was employed to acquire and analyze chromatographic data. The system was equipped with a Rheodyne injector with a 10- μL injection loop, and a Phenomenex Luna C18 (4.6 mm \times 150 mm, 5 μm) (Phenomenex, USA) analytical column. The separation was performed using acetonitrile (solvent A) and 0.1% acetic acid in water (solvent B) as mobile phase. The gradient program was as follows: 0–3 min, 40% solvent A; 3–4 min, ramped to 50% solvent A; 4–8 min, 50% solvent A; 8–9 min, ramped to 70% solvent A; 9–12 min, 70% solvent A; 12–13 min, ramped to 100% solvent A; 13–17 min, 100% solvent A; 17–18 min, decreased to 40% solvent A. A re-equilibration period of 2 min with 40% solvent A was carried out between individual runs. The detections were performed at 271 nm for Ph; 317 nm for 4NP; 258 nm for 24DNP; 276 nm for 2NP and 2CP; 280 nm for 4C3MP and 24DMP; 266 nm for 2M46DNP; 286 nm for 24DCP; and 288 nm for 246TCP.

Fourier transform infrared spectra (FTIR) were recorded on a TENSOR27 infrared scanner (Bruker, Germany) with a resolution of 2 cm^{-1} and a spectral range from 4000 to 400 cm^{-1} . The X-ray diffraction (XRD) patterns were recorded using an Empyrean X-ray diffractometer (XRD) (PANalytical, the Netherlands) with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) over the 2θ range from 5° to 50°. The morphology of MIL-101 was observed on dualbeam scanning electron microscope/focused ion beam (FIB-SEM) (FEI Helios NanoLab G3 CX Dual Beam, FEI, USA).

Other instruments were used in the procedure, including a vortex mixer model G560E (50 Hz) (Scientific Industries, USA), an ultrasonic cleaner (50/60 Hz) model B-220 (Branson, USA), a rotavapor model R-200 (Buchi Labortechnik AG, Switzerland), a centrifuge model Z206A (Hermle Labortechnik, Germany) and an oven model UN110 (Mettler, Germany).

2.3. Synthesis of the sorbent

The NH₂-MIL-101(Fe) sorbent was synthesized by solvothermal treatment adapted from the previously published procedure reported by S. Bauer et al. [30]. Briefly, a solution of 0.2250 g 2-aminoterephthalic acid in 7.5 mL DMF was mixed with a solution of 0.4050 g ferric chloride anhydrous in 7.5 mL DMF. The mixture was stirred for 10 min before thermal treatment in a stainless steel autoclave at 110 °C for 24 h. The product was filtered under vacuum, then washed with DMF and dried at room temperature. The MIL-101(Fe) was synthesized based on the procedure reported by Gecgel et al. [31] and was used for comparison of the extraction performance with the NH₂-MIL-101(Fe).

2.4. Extraction procedure

The determination of phenolic pollutants was carried out by D- μ SPE using amine-functionalized MOF (NH₂-MIL-101(Fe)) as sorbent followed by HPLC with photodiode array detector. For this purpose, an aliquot of 10.00 mL aqueous phenol standard or sample solution was added to a 15 mL centrifuge tube containing 50 mg of sorbent. The mixture was then placed in a vortex mixer for 10 s to accelerate the sorption of the target analytes onto the sorbent. Subsequently, the solid sorbent was isolated from the solution by centrifugation at 3100 $\times g$ for 1 min. After that, the supernatant was discarded. Then, 2.0 mL of 0.5% acetic acid/acetonitrile mixture was added in the centrifuge tube. The analytes were desorbed by vortex mixing for 10 s. The mixture was centrifuged at 3100 $\times g$ for 1 min. The desorption solvent which contained analytes of interest was filtered through 0.45 μm membrane and evaporated to dryness by rotary evaporator. The residue was reconstituted in 50 μL of acetonitrile before

further injecting to HPLC for analysis. The proposed D- μ SPE procedure is schematically depicted in Fig. 1.

3. Results and discussion

3.1. Sorbent characterization

The prepared NH₂-MIL-101(Fe) was characterized by XRD, SEM, and FTIR techniques. The framework structure of as-synthesized MIL-101 was identified by X-ray diffraction and the pattern is shown in Fig. 2. The XRD pattern of the as-synthesized sorbent was in good accordance with the simulated MIL-101, indicating that the pure phases were obtained. To identify the functional groups of NH₂-MIL-101(Fe), the FTIR spectroscopy was studied and the results are shown in Fig. 3. Strong bands at 1580 and 1433 cm⁻¹ correspond to the presence of the symmetrical and asymmetrical C–O stretching vibrations of carboxylates and indicate the presence of 2-aminoterephthalate anions in the framework. Moreover, a shoulder at 1623 cm⁻¹ attributed to the N–H bending and an absorption band at 1340 cm⁻¹ assigned to the C–N stretching of aromatic amines. SEM images in Fig. 4 show the morphology of NH₂-MIL-101(Fe). The prepared material consists of hexagonal microspindle crystals with about 0.9–1.5 μ m of the length, and 300–500 nm of the width. Therefore, the results of XRD, FTIR and SEM clearly confirm the formation of NH₂-MIL-101(Fe) structure.

3.2. Optimization of the DSPE condition

In the process of optimization experiments, aqueous standard solutions containing 5 mg L⁻¹ of each phenol were investigated. All experiments were carried out in triplicate. Percentage of extraction recovery (% ER) was evaluated and used as the experimental response. The extraction recovery was calculated according to the following equation:

$$\%ER = \left(\frac{V_f}{V_i}\right) \left(\frac{C_f}{C_i}\right) \times 100$$

Where V_i and V_f are the initial and final volumes, C_i is the initial concentration of analyte spiked in solution and C_f is the final concentration of analyte in solution that calculated from calibration curve [32].

3.2.1. Sorbent amount

In order to achieve a satisfactory extraction efficiency for the target analytes, the effect of the amount of NH₂-MIL-101(Fe) sorbent was studied by varying from 10 to 90 mg. Other experimental parameters were kept as follows: 10.00 mL sample volume, 10 s vortex adsorption time, 2 min centrifugation after adsorption, 0.5 mL of 0.5% acetic acid in

acetonitrile as desorption solvent, 10 s vortex desorption time, and 1 min centrifugation after desorption. As illustrated in Fig. 5, the extraction recovery increases with the increase of sorbent amount from 10 to 50 mg, and reaches the maximum plateau afterward. Therefore, 50 mg of sorbent material was sufficient for effective extraction of the target analytes in the studied concentration, and was adopted in the further experiments.

3.2.2. Type of desorption solvent

Choice of desorption solvent is one of crucial parameters in sorbent-based extraction method. To obtain high extraction recovery for the target analytes, 0.5 mL of various solvents, including methanol, acetonitrile, acetone, 0.5% acetic acid in methanol, 0.5% acetic acid in acetonitrile and 0.5% acetic acid in acetone, were studied for desorption of phenol compounds from the Fe-MIL-101-NH₂ sorbent. Vortex was applied for 10 s during desorption step in order to ensure sufficient interaction of the sorbent containing analytes with the desorption solvent. Other experimental conditions were kept as follows: 50 mg sorbent, 10.00 mL sample volume, and 2 min centrifugation after adsorption. The results in Fig. 6 indicated that the highest extraction recoveries of most analytes were achieved using 0.5% acetic acid in acetonitrile as desorption solvent. Addition of acetic acid also resulted in significant increase of extraction recoveries for 2M46DMP and 24DNP. Therefore, the mixture of 0.5% acetic acid in acetonitrile was chosen for the desorption process.

3.2.3. Desorption solvent volume

To determine the effect of desorption solvent volume, the volume of 0.5% acetic acid in acetonitrile was varied in the range of 0.5–2.5 mL, while keeping other conditions as follows: 50 mg sorbent, 10.00 mL sample volume, 10 s vortex adsorption time, 2 min centrifugation after adsorption, 10 s vortex desorption time, and 1 min centrifugation after desorption. It should be noted that in this experiment the eluate containing desorbed analytes was subsequently injected into the HPLC system without evaporation. The results in Fig. 7 showed that the extraction recoveries of most analytes increased with increasing the volume of desorption solvent from 0.5 to 2.0 mL and remained almost constant afterward. Therefore, 2.0 mL of 0.5% acetic acid in acetonitrile was selected for further optimization.

3.2.4. Vortex adsorption time

To ensure maximum adsorption of the target analytes on the solid sorbent, vortex agitation was applied during adsorption process and the vortex time was studied from 10 to 100 s using the sorbent amount of 50 mg, 10.00 mL sample volume, 1 min centrifugation after adsorption, 2.0 mL of 0.5% acetic acid in acetonitrile as desorption solvent, 10 s vortex

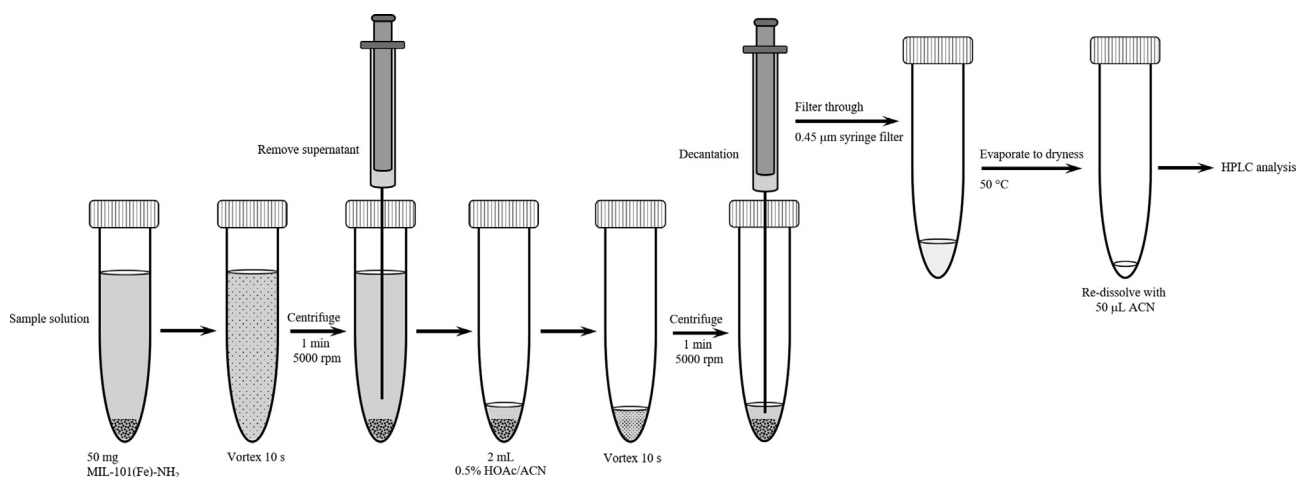


Fig. 1. Schematic diagram of the proposed D- μ SPE procedure for determination of phenolic pollutants.

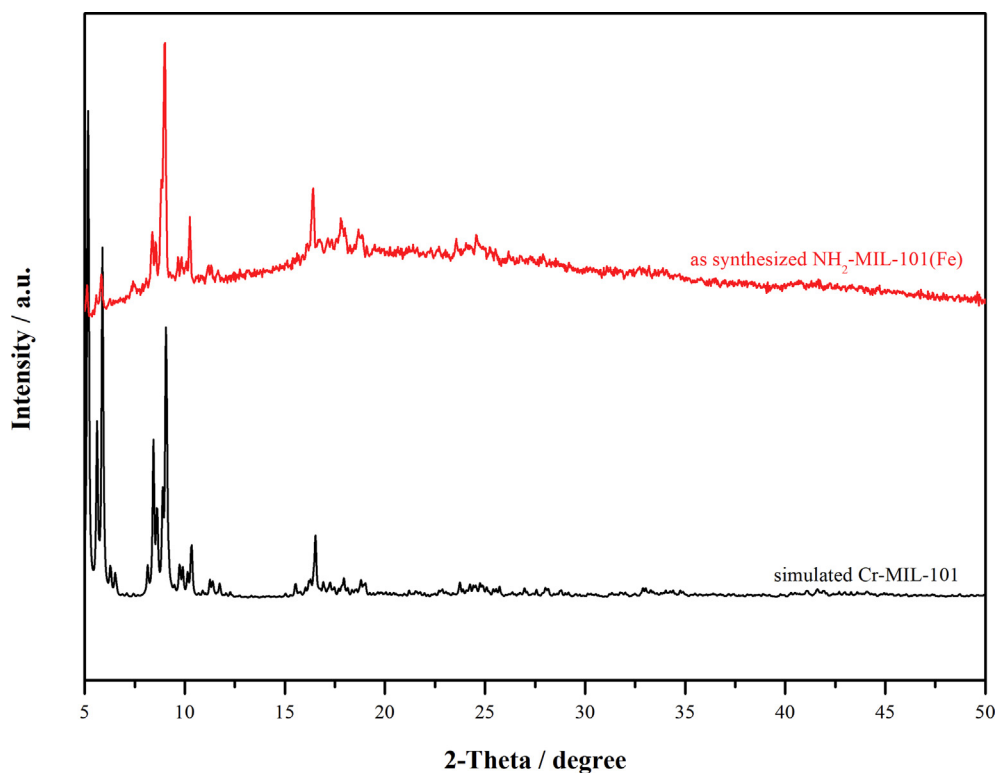


Fig. 2. XRD patterns of the synthesized NH₂-MIL-101(Fe) and simulated MIL-101.

desorption time, and 1 min centrifugation after desorption. It was found that extraction recoveries of the studies compounds increased significantly in case of using vortex when compared with those without vortex (see Fig. 8). However, vortex time from 10 to 100 s did not contribute to any improvement of extraction efficiency. Therefore, 10 s vortex was sufficient for adsorption process.

3.2.5. Centrifugation time after adsorption

In the present work, centrifugation was performed to separate the solid sorbent from the aqueous sample solution. The centrifugation time after adsorption process was varied in the range of 1–10 min. It could be observed that centrifugation for 1 min was enough for settle down the sorbent, as shown in Fig. 9. Therefore, the mixture was centrifuged for 1

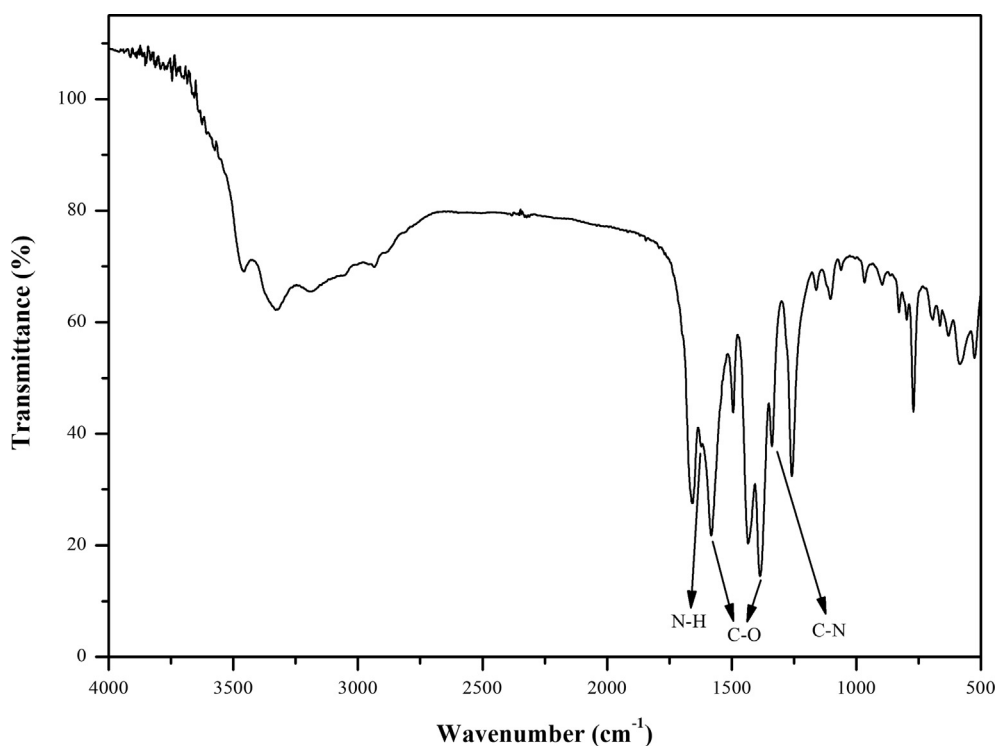


Fig. 3. FTIR spectra of the synthesized NH₂-MIL-101(Fe).

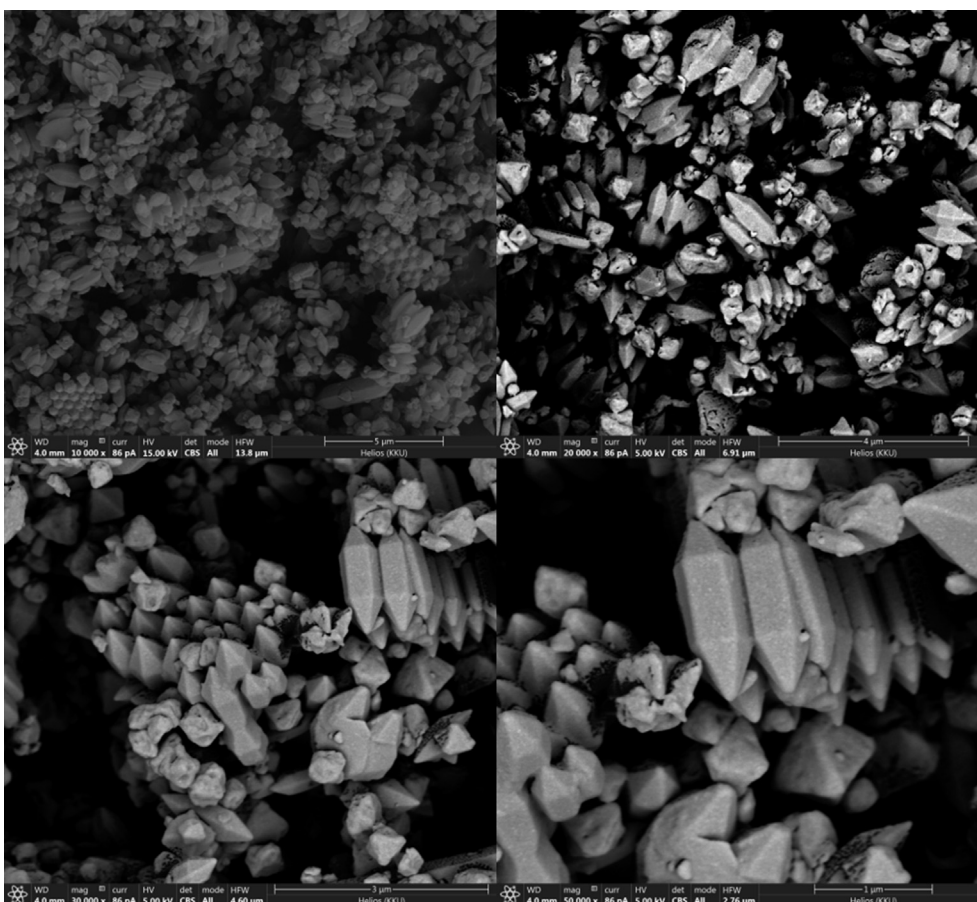


Fig. 4. SEM images of as-synthesized NH₂-MIL-101(Fe).

min after adsorption process before decanting the supernatant.

3.2.6. Vortex desorption time

In desorption process, the vortex time was also studied in the range

from 10 to 100 s, using 50 mg sorbent, 10.00 mL sample volume, 10 s vortex adsorption, 1 min centrifugation after adsorption, 2.0 mL of 0.5% acetic acid in acetonitrile as desorption solvent, and 1 min centrifugation after desorption. The highest extraction recoveries were obtained using

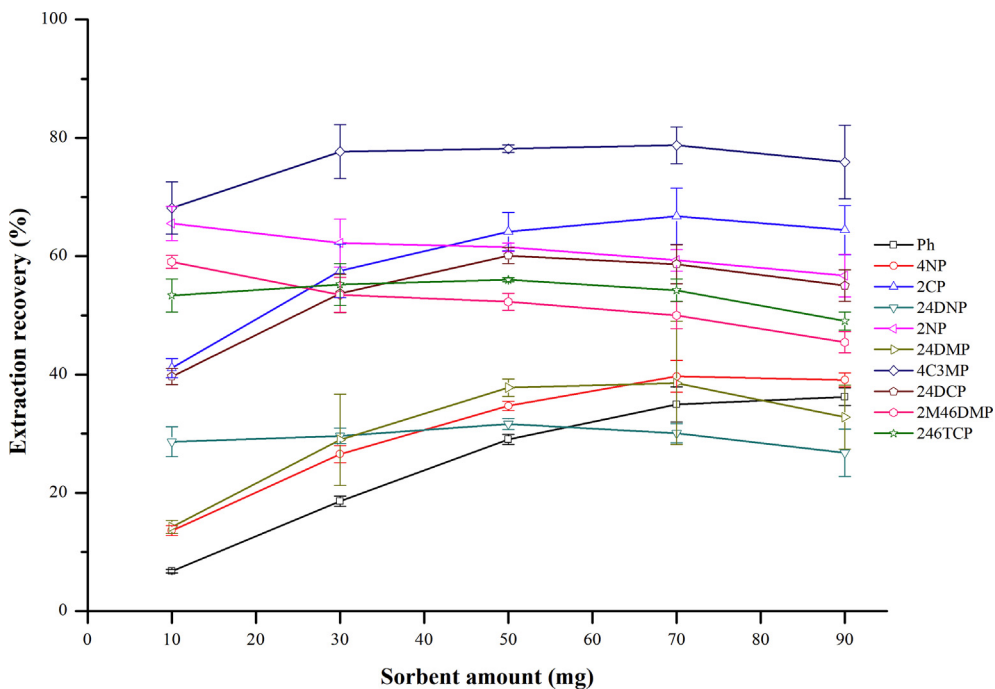


Fig. 5. Effect of sorbent amount on D- μ SPE of phenolic pollutants.

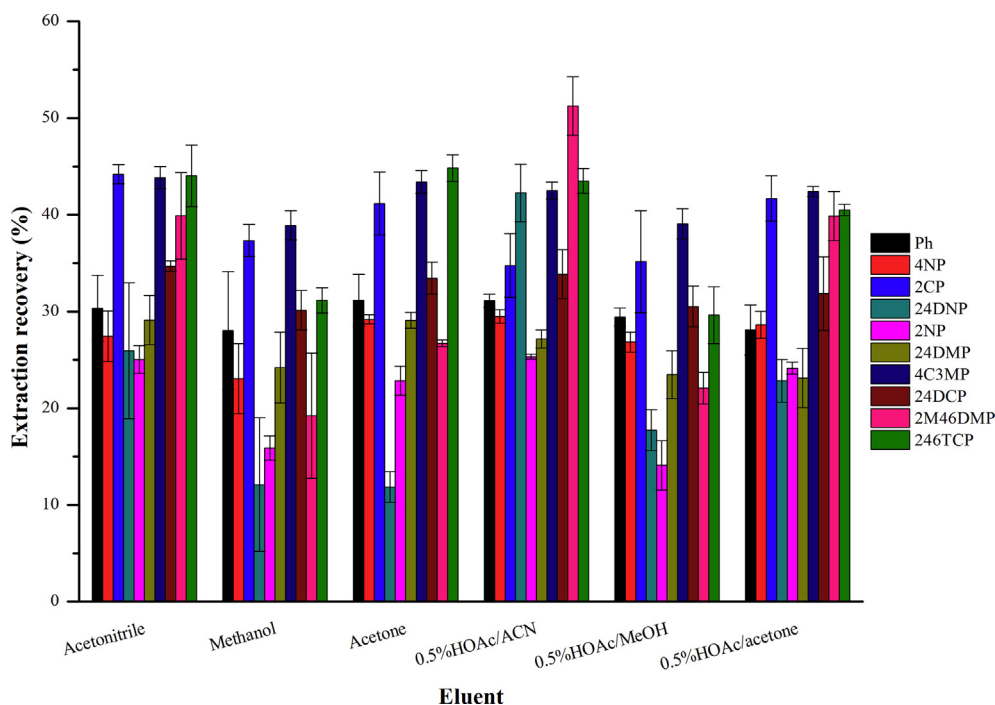


Fig. 6. Effect of eluent type on D- μ SPE of phenolic pollutants.

10 s vortex desorption, and remained constant beyond this point. In addition, it could be observed that the higher extraction recoveries were reached when applying vortex during desorption process compared with the experiments without vortex (Fig. 10). Therefore, in this work the vortex time of 10 s was selected during desorption process.

3.2.7. Centrifugation time for desorption

Different centrifugation time in the range of 1–10 min were studied for separation of the solid sorbent from the eluent. However, longer centrifugation did not improve the extraction recovery of the target analytes (Fig. 11). Therefore, centrifugation for 1 min was found to be

sufficient in this work.

In order to improve the pre-concentration ability of the proposed extraction procedure, evaporation and reconstitution were performed before analysis by HPLC. In this work, the eluate was evaporated at 55 °C to dryness and the residue was reconstituted in 50 μ L acetonitrile before subjecting to HPLC for further analysis. It was found that the higher enrichment factors were attained in the range of 26–120.

3.3. Analytical performance

Using the optimized conditions, the analytical performance of the

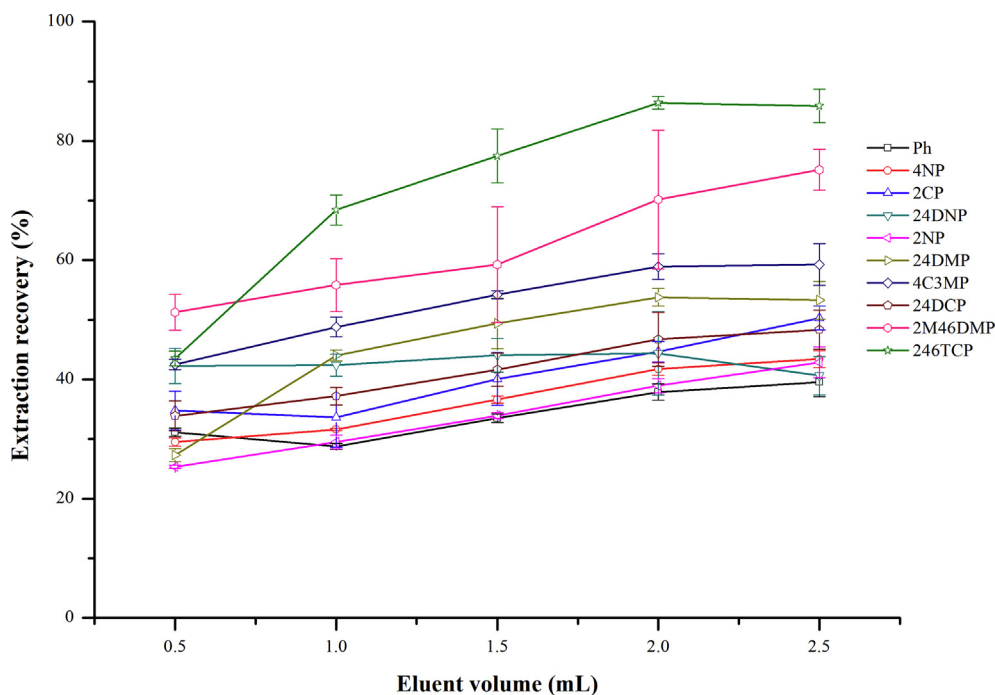


Fig. 7. Effect of eluent volume on D- μ SPE of phenolic pollutants.

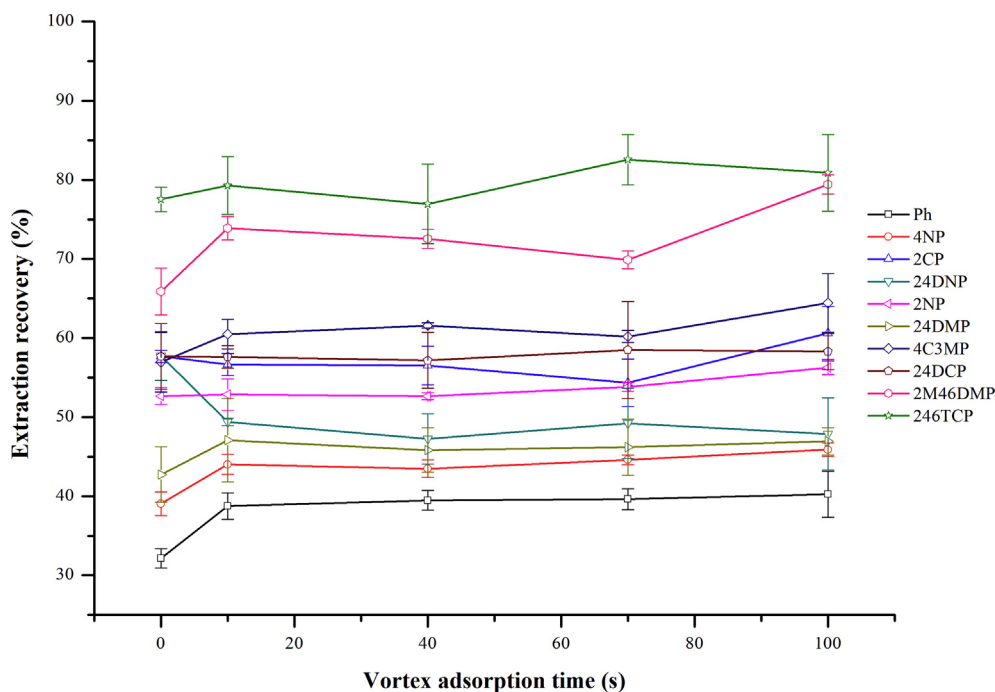


Fig. 8. Effect of vortex adsorption time on D- μ SPE of phenolic pollutants.

proposed D- μ SPE-HPLC-DAD procedure for quantification of phenolic pollutants was investigated including linearity, sensitivity in terms of limits of detection (LODs) and limits of quantification (LOQs), precision and accuracy. The analytical features of the proposed method are summarized in Table 1. The method exhibited good linearity of the calibration graphs in the range of 1.25–5000 $\mu\text{g L}^{-1}$ with the correlation coefficients of greater than 0.9900. The LODs and LOQs, which were calculated based on the signal-to-noise ratios of 3 and 10, respectively, were in the ranges of 0.4–9.5 $\mu\text{g L}^{-1}$ and 1.25–30 $\mu\text{g L}^{-1}$, respectively. The precision was evaluated in terms of the relative standard deviations (RSDs) of the intra- and inter-day experiments. By replicate analyses of

standard mixture of the analytes with the concentration at the LOQ of each compound (Ph, 30; 4NP, 4.7; 2CP, 30; 24DNP, 12.8; 2NP, 16; 24DMP, 25; 4C3MP, 15; 24DCP, 25; 2M46DNP, 1.25; 246TCP, 11.3 $\mu\text{g L}^{-1}$) in a day ($n = 8$) and several days ($n = 4 \times 3$), the RSDs of retention time and peak area were below 1.3% and 13.9%, respectively. The short extraction time of less than 3 min was attained in the proposed method. Chromatograms obtained from D- μ SPE-HPLC process was compared with that obtained by direct HPLC as shown in Fig. 12.

To study the inter-batch precision, the $\text{NH}_2\text{-MIL-101(Fe)}$ sorbent was synthesized in 3 different days and was tested as sorbent for extraction of phenol compounds. The %ER and %RSD were calculated. The results

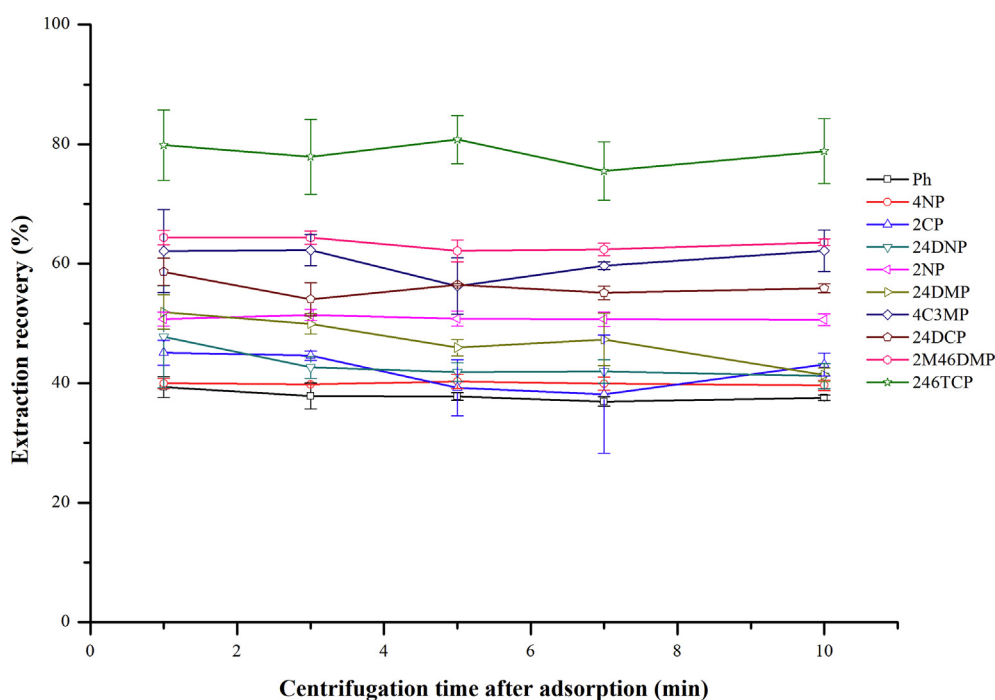


Fig. 9. Effect of centrifugation time after adsorption on D- μ SPE of phenolic pollutants.

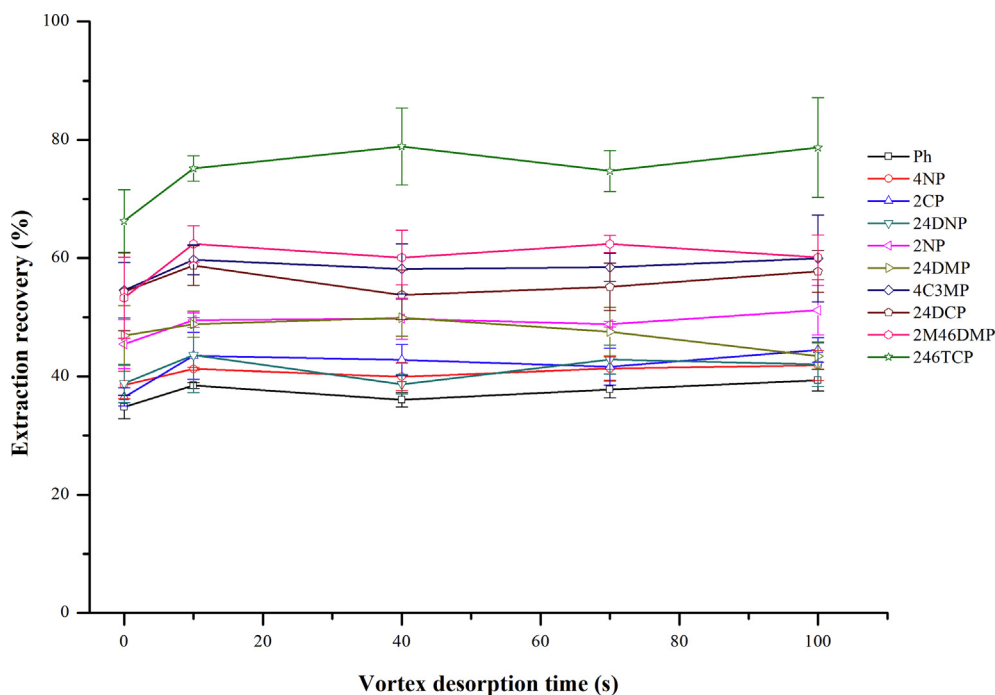


Fig. 10. Effect of vortex desorption time on D- μ SPE of phenolic pollutants.

showed good precision of the %ER with the RSDs of lower than 10%, as summarized in Table 1.

To demonstrate the stability of the synthesized MOF for extraction of phenol compounds in aqueous solution, the XRD patterns of MIL-101(Fe) before and after adsorption of phenol standards solution (2 mg L^{-1} each) were compared, as shown in Fig. 13. The obtained XRD patterns showed that it is obviously stable after extraction of phenol in aqueous solution. In the present work, the %ER ranged from 28 (Ph) to 89 (246TCP) were reached. Considering the extraction ability of the sorbent for the studied phenol compounds, 246TCP, 24DNP and 2M46DNP showed higher extraction recoveries than the other phenols, and the lowest extraction

was obtained for Ph. These results agree with those reported in our previous work using $\text{NH}_2\text{-MIL-53(Al)}$ as sorbent [20, 21]. The interaction between sorbent and substituted phenols are higher than that of Ph due to hydrogen bonding, dipole-dipole interaction and also $\pi\text{-}\pi$ interaction [7].

In order to investigate the performance of $\text{NH}_2\text{-MIL-101(Fe)}$ sorbent for extraction of phenol compounds, the sorbent was compared with MIL-101(Fe) without amino group. By the amine functionalization, it showed better adsorption ability than that of MIL-101(Fe) for most target analytes (see Fig. 14). This adsorption performance might be attributed to hydrogen bonding between some phenol compounds and the amino

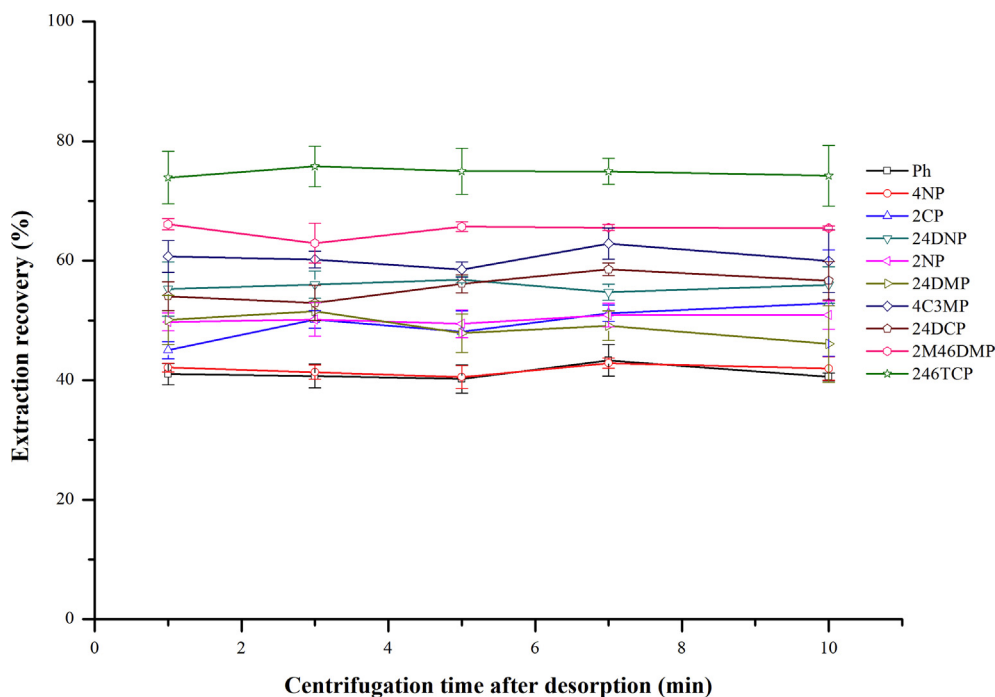


Fig. 11. Effect of centrifugation time after desorption on D- μ SPE of phenolic pollutants.

Table 1
Analytical features of the proposed D- μ SPE-HPLC method for determination of phenolic pollutants.

| Analyte | Linear range ($\mu\text{g L}^{-1}$) | Linear equation | R^2 | LOD ($\mu\text{g L}^{-1}$) | LOQ ($\mu\text{g L}^{-1}$) | EF ^a | %RSD ^b | | inter-day (n = 4 \times 3 days) | | inter-batch precision (n = 3) | | | |
|---------|---------------------------------------|---|--------------------|------------------------------|------------------------------|-----------------|-------------------|---------------|-----------------------------------|---------------|-------------------------------|-----------|------|-------|
| | | | | | | | intra-day (n = 8) | | t_R | Peak area | t_R | Peak area | % ER | % RSD |
| | | | | | | | t_R | Peak area | | | | | | |
| Ph | 30–1000 (1000–50000) | $y = 434195x + 6505$ ($y = 11005x - 4947$) | 0.9972 (0.9988) | 9.5 (250) | 30 (1000) | 40 | 0.7 (0.2) | 12.5 (6.4) | 0.5 (0.6) | 10.6 (6.2) | 28 | 9 | | |
| 4NP | 4.7–100 (500–50000) | $y = 4171324x + 11454$ ($y = 62222x - 31512$) | 0.9925 (0.9986) | 1.5 (100) | 4.7 (330) | 67 | 0.7 (0.4) | 5.1 (2.6) | 0.4 (0.7) | 10.6 (7.0) | 45 | 4 | | |
| 2CP | 30–1000 (2000–50000) | $y = 885032x - 11928$ ($y = 11131x - 3533$) | 0.9987 (0.9988) | 10 (500) | 30 (1670) | 80 | 0.4 (0.6) | 13.9 (3.6) | 0.4 (0.6) | 11.0 (7.6) | 42 | 4 | | |
| 24DNP | 15–1000 (500–50000) | $y = 1281523x + 21419$ ($y = 50238x - 4514$) | 0.9996 (0.9990) | 4 (100) | 12.8 (330) | 26 | 0.6 (0.7) | 4.6 (5.4) | 0.5 (1.0) | 11.9 (7.7) | 88 | 6 | | |
| 2NP | 16–5000 (1000–50000) | $y = 2017606x - 15557$ ($y = 33243x - 24251$) | 0.9900 (0.9976) | 5 (300) | 16 (1000) | 61 | 0.2 (0.5) | 8.2 (3.1) | 0.3 (0.5) | 10.3 (8.2) | 57 | 2 | | |
| 24DMP | 25–3000 (1500–50000) | $y = 558122x + 6173$ ($y = 10252x - 3358$) | 0.9962 (0.9976) | 7.5 (480) | 25 (1250) | 54 | 0.2 (0.5) | 8.1 (3.8) | 1.3 (0.4) | 8.6 (8.3) | 58 | 9 | | |
| 4C3MP | 15–1000 (1500–50000) | $y = 955857x + 10969$ ($y = 8685x - 4178$) | 0.999 (0.9987) | 4.5 (500) | 15 (1500) | 110 | 0.2 (0.5) | 5.4 (4.6) | 0.2 (0.5) | 9.5 (8.3) | 53 | 8 | | |
| 24DCP | 25–3000 (2000–50000) | $y = 992102x - 4502$ ($y = 10312x - 5976$) | 0.9999 (0.9986) | 7.5 (580) | 25 (1930) | 96 | 0.2 (0.5) | 9.3 (3.5) | 0.3 (0.5) | 9.4 (4.5) | 58 | 2 | | |
| 2M46DNP | 1.25–100 (150–50000) | $y = 5801394x + 33083$ ($y = 55835x - 8234$) | 0.9950 (0.9989) | 0.4 (50) | 1.25 (150) | 104 | 0.1 (0.8) | 7.3 (4.1) | 0.2 (0.7) | 12.2 (2.8) | 82 | 8 | | |
| 246TCP | 11.3–3000 (1500–50000) | $y = 991710x + 17020$ ($y = 8290x - 2913$) | 0.9996 (0.9979) | 3.5 (500) | 11.3 (1500) | 120 | 0.1 (0.4) | 10.4 (2.9) | 0.1 (0.3) | 11.5 (5.0) | 89 | 6 | | |

The values in parentheses were obtained from direct HPLC.

^a EFs were calculated by comparing the slope before and after D- μ SPE-HPLC.

^b Concentrations used for evaluation of the precision: Ph, 1000; 4NP, 330; 2CP, 1670; 24DNP, 330; 2NP, 1000; 24DMP, 1250; 4C3MP, 1720; 24DCP, 1930; 2M46DNP, 370; 246TCP, 2370 $\mu\text{g L}^{-1}$ for direct HPLC method, and Ph, 30; 4NP, 4.7; 2CP, 30; 24DNP, 12.8; 2NP, 16; 24DMP, 25; 4C3MP, 15; 24DCP, 25; 2M46DNP, 1.25; 246TCP, 11.3 $\mu\text{g L}^{-1}$ for D- μ SPE-HPLC method.

groups in $\text{NH}_2\text{-MIL-101(Fe)}$, as in agreement with previous report [6].

3.4. Application to real samples

The applicability of the proposed D- μ SPE method was investigated by analysis of four water samples collected from different sources in northeastern of Thailand. The samples were filtered through 0.45 μm membrane filter before analysis by the proposed D- μ SPE method. The studied samples did not contain the phenolic compounds. To evaluate the accuracy and the matrix effect on the established method, the recovery experiments were carried out by spiking two different concentration levels (near LOQs and 5 times as high as LOQs) of each phenol compound (level 1: Ph, 40; 4NP, 5; 2CP, 50; 24DNP, 15; 2NP, 20; 24DMP, 30;

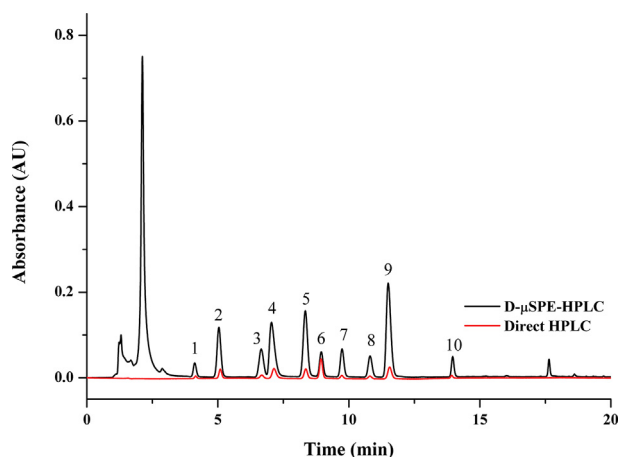


Fig. 12. Chromatograms obtained from direct HPLC and D- μ SPE-HPLC process. Peak assignment: 1, Ph; 2, 4NP; 3, 2CP; 4, 24DNP; 5, 2NP; 6, 24DMP; 7, 4C3MP; 8, 24DCP; 9, 2M46DNP; 10, 246TCP (concentration: 500 $\mu\text{g L}^{-1}$ for D- μ SPE-HPLC and 7000 $\mu\text{g L}^{-1}$ for direct HPLC).

4C3MP, 20; 24DCP, 30; 2M46DNP, 1.5; 246TCP, 15 $\mu\text{g L}^{-1}$, and level 2: Ph, 200; 4NP, 25; 2CP, 250; 24DNP, 75; 2NP, 100; 24DMP, 150; 4C3MP, 100; 24DCP, 150; 2M46DNP, 7.5; 246TCP, 75 $\mu\text{g L}^{-1}$) into the water samples. The results are summarized in Table 2. The range of mean recoveries was 68.4–114.4% with the RSDs of less than 14.3%.

3.5. Comparison of the proposed DSPE to other methods

The proposed D- μ SPE method using $\text{NH}_2\text{-MIL-101(Fe)}$ sorbent was compared to other extraction methods for determination of phenol compounds, as summarized in Table 3. The wide linear working ranges for determination of a variety of phenol compounds were observed using the developed method. The sensitivity in terms of LODs and LOQs is almost comparable to those obtained from other reports. The significant advantages of the proposed D- μ SPE are low consumption of sample

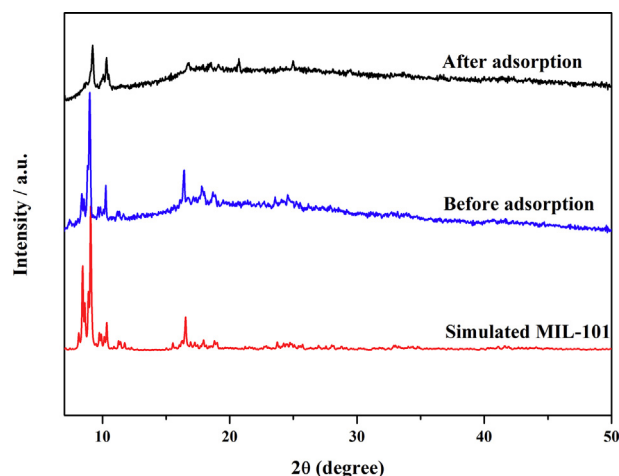


Fig. 13. XRD patterns of simulated MIL-101(Fe), MIL-101 (Fe) before and after adsorption of phenol standards in aqueous solution.

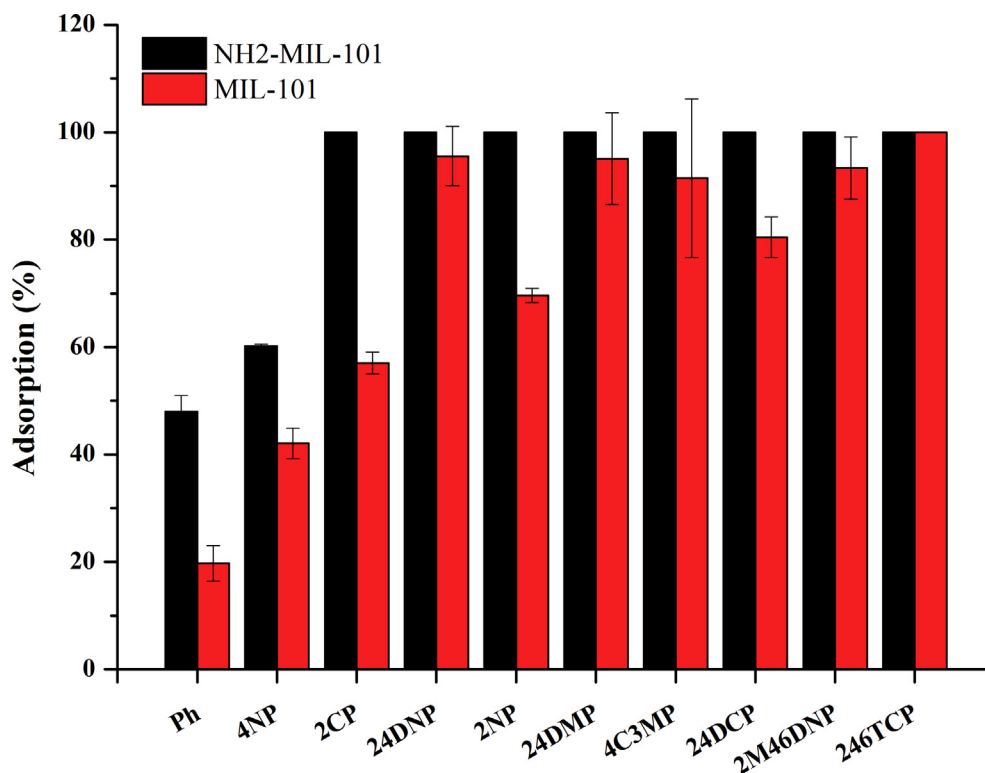


Fig. 14. Comparison of adsorption ability between NH₂-MIL-101(Fe) and MIL-101(Fe) using 2 mg L⁻¹ of each phenol standards.

Table 2
Determination of phenol residues in water samples.

| Analyte | Added (µg L ⁻¹) | Surface water I | | | Surface water II | | | Surface water III | | | River water | | |
|---------|-----------------------------|-----------------------------|-------|-------|-----------------------------|-------|-------|-----------------------------|-------|-------|-----------------------------|-------|-------|
| | | Found (µg L ⁻¹) | %R | % RSD | Found (µg L ⁻¹) | %R | % RSD | Found (µg L ⁻¹) | %R | % RSD | Found (µg L ⁻¹) | %R | % RSD |
| Ph | – | ND | – | – | ND | – | – | ND | – | – | ND | – | – |
| | 40 | 39.0 | 97.6 | 8.6 | 37.1 | 92.6 | 9.0 | 31.0 | 77.4 | 7.5 | 28.3 | 70.8 | 7.6 |
| | 200 | 194.0 | 97.0 | 7.0 | 202.7 | 101.4 | 9.8 | 191.9 | 95.9 | 13.3 | 163.1 | 81.6 | 8.5 |
| 4NP | – | ND | – | – | ND | – | – | ND | – | – | ND | – | – |
| | 5 | 4.8 | 96.5 | 8.3 | 4.3 | 87.0 | 7.4 | 5.3 | 105.3 | 12.1 | 3.7 | 74.6 | 11.1 |
| 2CP | 25 | 25.9 | 103.5 | 1.8 | 25.2 | 100.7 | 2.6 | 22.7 | 90.6 | 8.0 | 21.8 | 87.1 | 9.2 |
| | – | ND | – | – | ND | – | – | ND | – | – | ND | – | – |
| 24DNP | 50 | 53.7 | 107.3 | 4.0 | 51.0 | 101.9 | 1.7 | 42.9 | 85.9 | 8.9 | 48.4 | 96.9 | 10.0 |
| | 250 | 252.8 | 101.1 | 6.4 | 255.2 | 102.1 | 9.7 | 181.5 | 72.6 | 0.7 | 264.2 | 105.7 | 10.9 |
| 2NP | – | ND | – | – | ND | – | – | ND | – | – | ND | – | – |
| | 15 | 11.8 | 79.0 | 10.5 | 15.3 | 101.9 | 0.7 | 14.9 | 99.5 | 7.6 | 15.1 | 100.4 | 9.3 |
| 24DMP | 75 | 78.2 | 104.2 | 4.5 | 81.6 | 108.8 | 1.9 | 62.7 | 83.6 | 3.1 | 52.6 | 70.2 | 1.3 |
| | – | ND | – | – | ND | – | – | ND | – | – | ND | – | – |
| 24DCP | 20 | 18.6 | 93.0 | 2.8 | 19.7 | 98.4 | 6.2 | 14.7 | 73.7 | 4.0 | 19.0 | 95.1 | 1.2 |
| | 100 | 108.9 | 108.9 | 1.3 | 98.2 | 98.2 | 10.1 | 68.4 | 68.4 | 1.3 | 98.7 | 98.7 | 10.9 |
| 4C3MP | – | ND | – | – | ND | – | – | ND | – | – | ND | – | – |
| | 30 | 26.1 | 87.1 | 1.1 | 28.4 | 94.8 | 8.4 | 27.6 | 91.9 | 4.7 | 31.4 | 104.8 | 4.0 |
| 246TCP | 150 | 163.2 | 108.8 | 5.4 | 157.6 | 105.1 | 9.6 | 116.8 | 77.8 | 10.5 | 136.6 | 91.1 | 5.6 |
| | – | ND | – | – | ND | – | – | ND | – | – | ND | – | – |
| 2M46DNP | 20 | 16.9 | 84.6 | 3.2 | 17.8 | 89.1 | 0.4 | 18.9 | 94.4 | 1.6 | 16.0 | 79.8 | 3.0 |
| | 100 | 98.5 | 98.5 | 1.9 | 98.6 | 98.6 | 4.0 | 111.1 | 111.1 | 2.4 | 92.5 | 92.5 | 5.6 |
| 246TCP | – | ND | – | – | ND | – | – | ND | – | – | ND | – | – |
| | 30 | 29.3 | 97.6 | 4.0 | 26.3 | 87.6 | 7.8 | 23.9 | 79.7 | 7.9 | 26.7 | 88.9 | 5.2 |
| 246TCP | 150 | 151.3 | 100.9 | 7.2 | 149.0 | 99.3 | 4.1 | 125.6 | 83.7 | 4.8 | 114.0 | 76.0 | 12.5 |
| | – | ND | – | – | ND | – | – | ND | – | – | ND | – | – |
| 246TCP | 1.5 | 1.4 | 95.7 | 1.7 | 1.5 | 97.0 | 2.5 | 1.7 | 114.4 | 8.1 | 1.2 | 82.0 | 0.1 |
| | 7.5 | 7.4 | 98.0 | 7.1 | 7.0 | 93.6 | 3.7 | 6.2 | 82.3 | 6.0 | 7.3 | 97.4 | 0.2 |
| 246TCP | – | ND | – | – | ND | – | – | ND | – | – | ND | – | – |
| | 15 | 13.6 | 90.9 | 4.2 | 14.1 | 93.7 | 2.4 | 11.5 | 76.4 | 8.8 | 10.6 | 70.8 | 14.3 |
| | 75 | 78.1 | 104.2 | 0.2 | 79.4 | 105.8 | 1.0 | 85.7 | 114.3 | 2.7 | 71.9 | 95.8 | 8.9 |

ND: not detected refers to values below detection limits.

Table 3
Comparison of the proposed D- μ SPE to other extraction methods for determination of phenol compounds.

| Method [Ref] | Analytes | Sample | Extraction conditions | Analytical technique | Analytical performance |
|----------------------------|---|-------------------------|--|----------------------|---|
| VA-D- μ -SPE [20] | Ph, 4NP, 24DNP, 2NP, 4C3MP, 24DCP, 2M46DNP, 246TCP | Water | Sorbent: 30 mg NH ₂ -MIL-53(Al) MOF Sample volume: 10 mL Adsorption: 10 s vortex Eluent: 1.5 mL ACN-HOAc (9.5:0.5 v/v) Desorption: 10 s vortex | HPLC-DAD | Linear range: 1.5–10000 $\mu\text{g L}^{-1}$ LODs: 0.4–13.3 $\mu\text{g L}^{-1}$ LOQs: 1.3–51.9 $\mu\text{g L}^{-1}$ EFs: 45–105 %R: 72.3–111.4 RSDs: < 10.4% |
| SI-VA-D- μ -SPE [21] | Ph, 2CP, 24DMP, 4C3MP, 24DCP | Water | Sorbent: NH ₂ -MIL-53(Al) MOF suspension (1.50 mL of 0.64 g sorbent/16 mL water) Sample volume: 10 mL Adsorption: 1 min vortex, 2 min centrifugation Eluent: 500 μL acetone | HPLC-UV | Linear range: 100–10000 $\mu\text{g L}^{-1}$ LODs: 30–55 $\mu\text{g L}^{-1}$ LOQs: 90–150 $\mu\text{g L}^{-1}$ EFs: 5–14 %R: 83.0–122.4 RSDs: < 7.85% |
| In-syringe extraction [29] | Ph, 4NP, 2NP, 3MP, 4C3MP, 24DCP, 2M46DNP, 246TCP, PCP | River water | Sorbent: 5 mg graphene aerosols filled in 2-mL syringe Sample volume: 40 mL Adsorption: 20 min Eluent: 200 μL ACN | HPLC-UV | Linear range: 0.05–20 $\mu\text{g L}^{-1}$ LODs: 0.016–0.075 $\mu\text{g L}^{-1}$ LOQs: 0.053–0.250 $\mu\text{g L}^{-1}$ %R: 96.3–102.4 RSDs: < 5.4% |
| Online MMD-SPE [33] | 4NP, 2CP, 24DNP, 2NP, 24DMP, 4C3MP, 24DCP | Groundwater | Sorbent: polyvinylidene fluoride matrix disks containing entrapped UiO-66-NH ₂ MOFs Sample volume: 1.5 mL Eluent: 0.3 mL acetone Desorption flow rate: 0.5 mL min ⁻¹ | HPLC-DAD | Linear range: 0.5–500 $\mu\text{g L}^{-1}$ LODs: 0.1–0.2 $\mu\text{g L}^{-1}$ EFs: 12–20 %R: 90–98 RSDs: 3.9–5.7% (intraday), 4.7–5.7% (interday) |
| DSPE [34] | Ph, 4NP, 2CP, 24DNP, 2NP, 24DMP, 4C3MP, 24DCP, 2M46DNP, 246TCP, PCP | River water | Sorbent: 6.0 mg LDO-HSs Sample volume: 100 mL Eluent: 200 μL 10% TFA | HPLC-DAD | Linear range: 0.05–40 $\mu\text{g L}^{-1}$ LODs: 0.005–0.153 $\mu\text{g L}^{-1}$ LOQs: 0.018–0.507 $\mu\text{g L}^{-1}$ EFs: 36–459 %R: 93.9–124 RSDs: < 6.7% |
| MSPE [35] | 2CP, 3CP, 23DCP, 34DCP | Tap water and honey tea | Sorbent: 150 mg Zn/Co _{7:1} -MPC Sample volume: 100 mL Extraction time: 20 min shaking Eluent: 0.4 mL of 1% alkaline methanol | HPLC-UV | Linear range: 0.5–100 $\mu\text{g L}^{-1}$ LODs: 0.1–0.2 $\mu\text{g L}^{-1}$ %R: 83.0–114.0 RSDs: 5.7–8.7% |
| D- μ SPE [This study] | Ph, 4NP, 2CP, 24DNP, 2NP, 24DMP, 4C3MP, 24DCP, 2M46DNP, 246TCP | Surface water | Sorbent: 50 mg NH ₂ -MIL-101(Fe) Sample volume: 10.00 mL Adsorption: 10 s vortex, 1 min centrifugation Eluent: 2.0 mL 0.5% HOAc/ACN Desorption: 10 s vortex, 1 min centrifugation | HPLC-DAD | Linear range: 1.25–5000 $\mu\text{g L}^{-1}$ LODs: 0.4–9.5 $\mu\text{g L}^{-1}$ LOQs: 1.25–30 $\mu\text{g L}^{-1}$ EFs: 26–120 %R: 68.4–114.4 RSDs: < 13.9% |

volume and short extraction time. In addition, the NH₂-MIL-101(Fe) sorbent used in this work could be simply prepared when compared with previously reported sorbents [20, 21].

4. Conclusion

In the present work, a simple and effective sample preparation procedure based on DSPE for the determination of ten phenolic pollutants was proposed. NH₂-MIL-101(Fe) material was explored as sorbent and the D- μ SPE experimental conditions were optimized. The analytical characteristics of the method made it an appropriate sample pretreatment strategy to determine the target analytes in real samples.

Declarations

Author contribution statement

Rodjana Burakham: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Tittaya Boontongto: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed

reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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