

JOURNAL OF SEPARATION SCIENCE

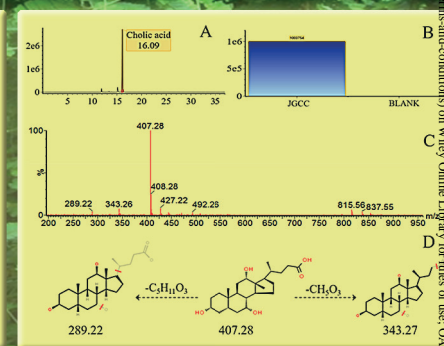
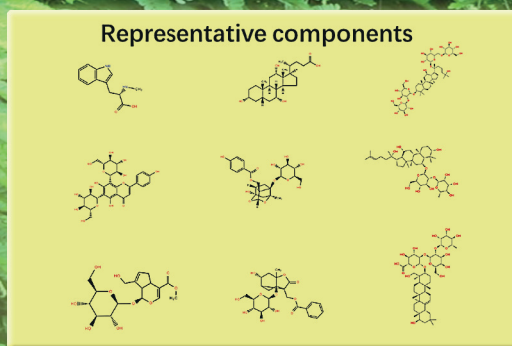
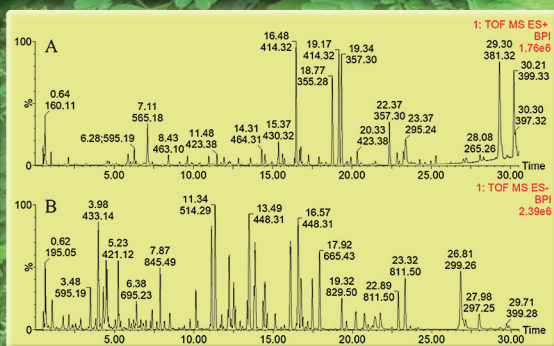
3 | 2022

Jigucuo capsule
A famous Chinese patent medicine



LC-MS/MS

Qualitative Analysis



Methods

Chromatography · Electroseparation

Applications

Biomedicine · Foods · Environment

www.jss-journal.com

WILEY-VCH

RESEARCH ARTICLE

Extraction of parabens by melamine sponge with determination by high-performance liquid chromatography

Jingkang Li¹ | Yanxiao Jiang² | Ying Sun¹  | Xinghua Wang¹  | Pinyi Ma¹ |
Daqian Song¹  | Qiang Fei¹ 

¹ Department of Analytical Chemistry, College of Chemistry, Jilin Province Research Center for Engineering and Technology of Spectral Analytical Instruments, Jilin University, Changchun, P. R. China

² School of Marine Science and Technology, Harbin Institute of Technology at Weihai, Weihai, P. R. China

Correspondence

Qiang Fei, College of Chemistry, Jilin Province Research Center for Engineering and Technology of Spectral Analytical Instruments, Jilin University, Qianjin Street 2699, Changchun, 130012, P. R. China.

Email: feiqiang@jlu.edu.cn

Funding information

National Natural Science Foundation of China, Grant/Award Numbers: 22074052, 22004046; Science and Technology Developing Foundation of Jilin Province of China, Grant/Award Number: 20200404173YY

In the present study, we propose a novel method for the extraction of parabens in personal care products. A new, simple adsorptive material was obtained by combining metal-organic frameworks and melamine sponges using the adhesive property of polyvinylidene fluoride. This new material, metal-organic frameworks/melamine sponges, was found to be particularly suitable for solid-phase extraction. The structural characteristics of metal-organic frameworks/melamine sponges were first analyzed by scanning electron microscopy. Subsequently, solid-phase extraction was performed on sample solutions, and the extracted substances were then analyzed by high-performance liquid chromatography. Following optimization of important experimental conditions, excellent recovery rates were obtained. Our novel method was then applied to the extraction of four parabens (methylparahydroxybenzoates, ethylparahydroxybenzoates, propylparahydroxybenzoates, and butylparahydroxybenzoates) from real samples. The results yielded limits of detection of 0.26–0.41 ng/mL. The inter- and intra-day recoveries were 104.0–109.7% and 91.2–98.1%, respectively (relative standard deviation, <13.8%).

KEYWORDS

melamine sponges, metal-organic frameworks, parabens, personal care products, solid-phase extraction

1 | INTRODUCTION

Parabens, also known as *p*-hydroxybenzoates [1], include methyl-, ethyl-, propyl-, and butyl- esters of *p*-hydroxybenzoic acid [2,3]. Because of their excellent antibacterial properties [2], parabens are widely used as a preservative in personal care products, cosmetics, foods, health care products, and pharmaceuticals [4]. With recent trends in society and improvements in life quality, there has been an increasing demand among men and

women for personal care products and cosmetics [5,6]. However, parabens are weak endocrine disruptors that can interfere with the function of endogenous hormones by binding to estrogen receptors [7,8]. Hence, the use of *p*-hydroxybenzoates in cosmetics is usually regulated. EU regulations permit *p*-hydroxybenzoate levels up to a concentration of 0.4% for a single ester and 0.8% for ester mixtures [9]. In the present study, we propose a rapid detection method for parabens in personal care products.

Metal-organic frameworks (MOFs) are porous materials composed of metal clusters and organic species [10]. Different MOFs can be characterized by their unique network of holes [11]. Because MOFs demonstrate several important advantages over other materials, including an

Article Related Abbreviations: MeS, melamine sponges; MOF, metal-organic framework; PVDF, polyvinylidene fluoride; XRD, X-ray powder diffraction

adjustable aperture, a large surface area, and a flexible structure, they can potentially be used in important applications such as gas storage, separation, catalysis, and drug release [12,13]. In the field of analytical chemistry, MOFs are considered a promising sample preparation material [14]. Indeed, MOFs are increasingly used for the extraction or adsorption removal of various toxic organic substances in the liquid phase [15]. According to traditional methods, MOFs can be directly placed into the water sample for dispersed SPE [16]. MOFs demonstrate excellent adsorption capacity for the target when placed in full contact with the sample [17]. However, traditional dispersed SPE methods are associated with significant loss of MOFs (especially following centrifugation and filtration), and such methods can be quite time-consuming [18].

Recently, numerous studies have reported that functional materials can be combined with melamine sponges (MeS) to facilitate oil-water separation [19–21]. MeS is a foam-like material comprised of formaldehyde-melamine-sodium bisulfite copolymer [22]. Its porous structure (>99%) and its easily modified frame make MeS a suitable adsorption material [23,24]. In addition, the unique structure of MeS facilitates rapid target removal from the aqueous phase, promoting efficient and rapid adsorption of contaminants [25]. However, the functionalization process for foam materials is relatively cumbersome, requiring specialized equipment [21]. Here, we propose a novel method for the preparation of metal-organic framework functionalized sponges for use as an extraction material, markedly shortening the whole sample processing process. To date, the application of MIL-68(Al)/ polyvinylidene fluoride (PVDF) functionalized sponge material for the simultaneous extraction of multi-residues of parabens in cosmetics has not previously been reported.

In the present study, we combine the advantages of MeS and MIL-68(Al), exploiting the adhesive property of PVDF to bind MIL-68(Al) to MeS through physical encapsulation [23]. Our novel MIL-68(Al)/MeS column was then used as an adsorbent for the extraction of parabens from personal care products [26]. After extraction, the target analytes were detected by HPLC. In comparison with traditional extraction methods, our novel extraction method demonstrates a higher recovery and increased convenience [27,28].

2 | MATERIALS AND METHODS

2.1 | Preparation of MOFs-coated MeS

Reagents and instruments information can be found in Supporting Information. MIL-68(Al) was synthesized according to the reported method [29]; the synthesis steps can be found in Supporting Information. To prepare blank

MeS columns, the MeS was first cut into sponge columns ($d = 7$ mm, $h = 2$ cm) using a punch. MeS columns were then washed three times with methanol and deionized water to eliminate impurities, and finally dried at 308 K in an oven for 12 h. To prepare MIL-68(Al)/MeS (Figure 1), 150 mg of MIL-68(Al) powder was dispersed in 5 ml of acetone under ultrasound for 25 min [23]. PVDF solution (1.1 g, 7.5 wt.% in *N,N*-dimethylformamide) was then added to the bottle containing MIL-68(Al)/acetone composite, and the suspension was ultrasonicated for 30 min to obtain the uniform coating solution [30,31]. Next, approximately 600 μ l of the final uniform suspension was transferred to a silicone ice cube mold ($1 \times 1 \times 1$ cm). The blank MeS column was then placed in the mold to adsorb the coating solution. Finally, the functionalized MeS columns were transferred to a surface dish and dried at 358 K for 12 h.

2.2 | Sample preparation

The samples (50 mg) were dissolved in 2 mL ACN, diluted in a 500 mL volumetric flask with ultrapure water [32], and stored in a clean bottle at 277 K in the dark for subsequent use.

2.3 | SPE procedure

Figure S1 demonstrates the extraction procedure. First, 5 mL of the sample solution (pH = 5, 0% salt concentration) and 20 μ L standard solution (20 ng/mL) were mixed in a 10 mL centrifuge tube. The centrifuge tube was then shaken for 3 min to ensure thorough mixing of the solution. Next, a MIL-68(Al)/MeS column was added to the centrifuge tube, and the tube was vortexed for 12 min to facilitate adsorption of the target. After adsorption, the column was removed from the solution, squeezed with tweezers to aid solution removal. The sponge can no longer be squeezed out of droplets, and then placed into a centrifuge tube containing 3 mL of desorption solvent. This centrifuge tube was vortexed for 12 min, and the target analyte was eluted with ACN. Finally, the solution containing the target analyte was dried under nitrogen at 313 K, then re-dissolved in 100 μ L of ACN and filtered through a 0.22 μ m nylon membrane for HPLC analysis.

3 | RESULTS AND DISCUSSION

3.1 | Characterization

Three representative MOFs were used to modify the blank sponge: MIL-101(Cr), HKUST-1(Cu), and MIL-68(Al).

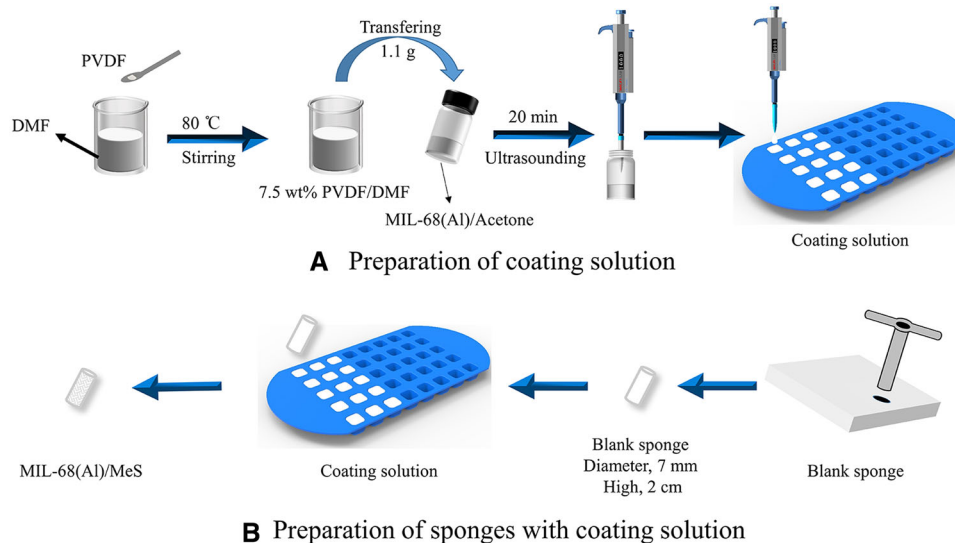


FIGURE 1 Schematic illustrating the preparation of MIL-68(Al)-coated melamine sponge

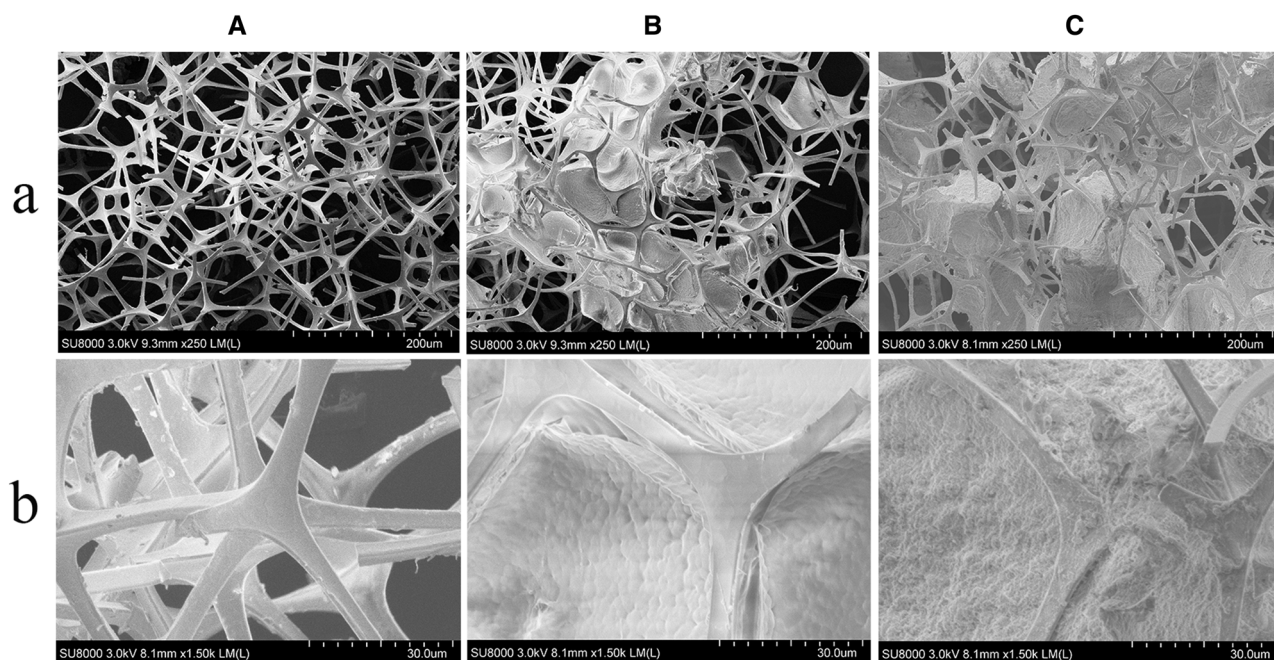


FIGURE 2 (A) SEM images of blank sponge. (B) SEM images of sponge loaded with polyvinylidene fluoride (PVDF). (C) SEM images of sponge loaded with MIL-68(Al) and PVDF. (A) and (B) represent SEM images with different multiples

The specific synthesis procedures can be found in the Supporting Information. The morphological characteristics of the functionalized sponges were first evaluated by SEM. SEM images of blank MeS at different multiples are shown in Figure 2A. The MeS skeleton can be clearly seen under high power. SEM images of MeS modified with PVDF at different multiples are shown in Figure 2B. These images reveal that PVDF attachment to the pores and the skeleton resembles fish scales. Finally, SEM images of 150 mg MIL-68(Al)/MeS at different multiples are shown

in Figure 2C. These images reveal the load distribution of MOFs. While MOFs were mainly distributed on the PVDF between pores, some were evenly distributed on the skeleton. This result is consistent with the final uniform extraction performance. In contrast, the MOFs of HKUST-1(Cu) demonstrate a large particle size, and the load distribution is not uniform (Figure 3B). Because MIL-101(Cr) (Figure 3A) and MIL-68(Al) (Figure 3C) were more evenly distributed throughout the sponge skeleton, the characteristics of these MeS/MOFs columns were

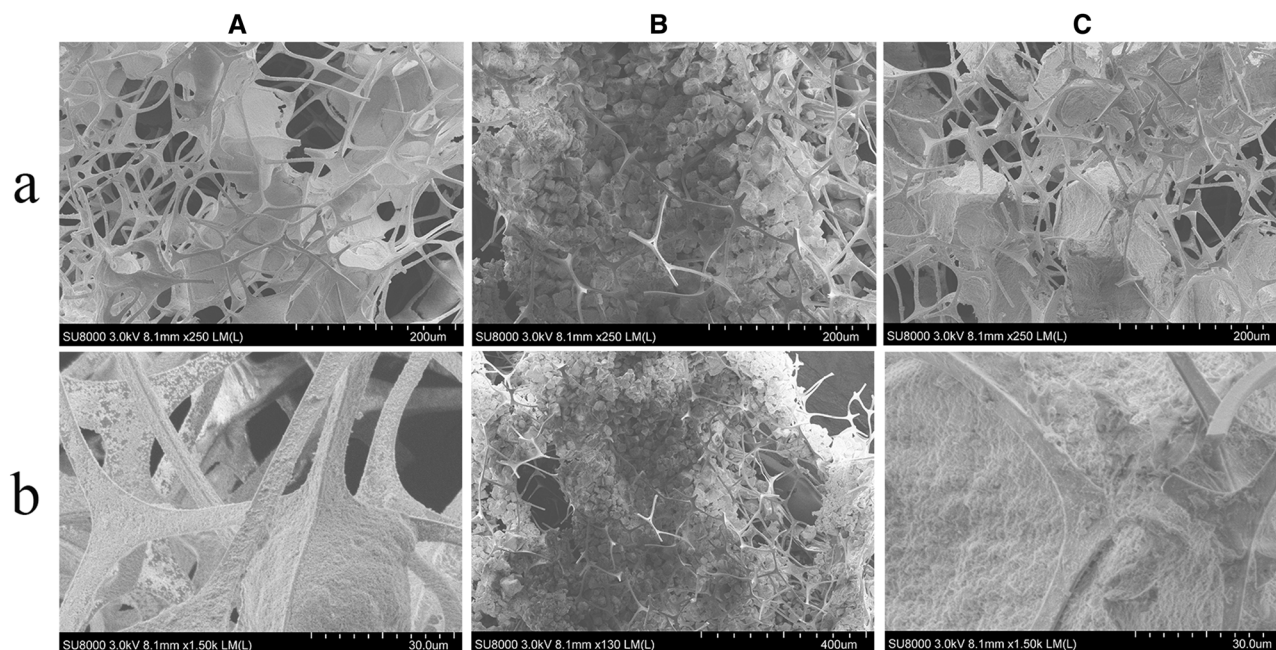


FIGURE 3 SEM images of sponge-column-modified metal-organic frameworks (MOFs). (A) MIL-101(Cr). (B) HKUST-1(Cu). (C) MIL-68(Al). SEM images are shown at different magnifications (A,B)

more conducive for subsequent experiments. MIL-68(Al) performs best in practical application.

The characteristics of MIL-68(Al) were next evaluated using X-ray powder diffraction (XRD) and N_2 adsorption isotherm. The XRD pattern for MIL-68(Al) is demonstrated in Figure S2A (with the corresponding SEM image of MIL-68(Al) shown in the inset). The characteristic peaks of MIL-68(Al) are in accordance with previous reports. The permanent porosity of MOF material was also evaluated in an N_2 adsorption isotherm experiment at 77 K (Figure S2B). The Brunauer-Emmett-Teller adsorption surface area and pore parameter (V_{pore}) of the prepared MIL-68(Al) were $1171.6 \text{ m}^2/\text{g}$ and $0.8 \text{ cm}^3/\text{g}$, respectively. Moreover, FTIR spectroscopy was also carried out on the three synthesized MOFs (Figure S2C). In the FTIR spectrum, strong peaks around 3400 cm^{-1} were ascribed to the stretching band of $-\text{OH}$ groups. Peaks at $1650\text{--}1430 \text{ cm}^{-1}$ corresponded to COO^- stretching vibration, and C-C stretching vibration of benzene, which demonstrated the presence of the carboxylate linker of MOFs.

3.2 | Selection of MOFs/MeS

In preparation for experimental use, the extraction performance of the MOFs was determined. As shown in Figure S3A, the performance of MIL-68(Al) was superior to that of the other two MOFs. Therefore, MIL-68(Al) was selected for further evaluation as an extractor. In addition, the results demonstrate the inherent adsorption capac-

ity of MeS, thus confirming the utility of this material for extraction. Moreover, MeS has previously been applied for the determination of *p*-hydroxybenzoate in cosmetics [26]. Under the methodological conditions reported in our study, the recovery rates are between 73.25 and 104.23%.

As shown in Figure S3B, recovery rates initially increase with the amount of coating but eventually reach a maximum. The maximum recovery rate was achieved at a load mass of 125 mg (with no significant change observed at higher load masses). It reached a stable equilibrium at 150 mg that was selected as an appropriate loading mass.

3.3 | Optimization of the proposed extraction procedure

3.3.1 | Effects of pH on extraction

pH is well known to have a marked influence on SPE experiments and the structure of MOFs. To explore the application range of our MIL-68(Al)/MeS columns, samples were selected for comparison from pH 3 to 11. As shown in Figure S4A, the novel material demonstrated good adsorption and extraction characteristics in the pH 3–7 and pH 7–11 (alkaline) ranges. According to previous reports, MOFs synthesized with terephthalic acid as an organic ligand collapse under strongly alkaline conditions and subsequently decompose [33]. As revealed in the SEM image in Figure 3C, MIL-68(Al) is generally enveloped and protected by the PVDF, and is primarily located in the

pores (as opposed to the skeleton). While acceptable target recoveries were achieved throughout the pH 3–11 range, optimum recovery was achieved at pH 5. Therefore, pH 5 was selected for all subsequent experiments.

3.3.2 | Effects of salt concentration on extraction

The concentration of salt is an important factor in many chromatographic experiments. In particular, “salting-out” may result in a reduction in the solubility of the target analyte in solution, thus affecting the extraction performance. In previous studies, the effects of salt concentration on extraction performance were evaluated after the addition of NaCl [34]. Here, the performance of MIL-68(Al)/MeS columns was evaluated at eight different salt concentrations (range, 0–350 mg) (Figure S4B). The results reveal that the extraction recoveries of all parabens were significantly reduced in the presence of salt (in comparison with the recoveries of samples in the absence of salt). Thus, no salt was added in subsequent experiments.

3.3.3 | Vortex extraction time

In our extraction experiments, the time of adsorption extraction is equal to the vortex time. Therefore, the vortex time can be expected to have a marked influence on the extraction experiment. As shown in Figure 4A, target recovery demonstrated a maximum at a vortex time of 12 min, with recoveries at shorter vortex times showing a downward trend. At vortex times longer than 12 min, the curve fluctuated below the maximum value, with little change. Therefore, 12 min was selected as the optimal extraction vortex time.

3.3.4 | Type and the volume of elution solvent

The choice of elution solvent had a marked influence on target recovery. Target recoveries in methanol, ACN, *n*-hexane, acetone, and diethyl ether are reported in Figure 4B. Recovery was particularly dependent on the polarity of the solvent. As shown in Figure 4C, recovery in ACN was higher than recovery in other elution solvents. While methanol demonstrated slightly lower recovery than ACN, *n*-hexane was the least effective. Therefore, ACN was selected as the eluting solvent in subsequent experiments.

To determine an appropriate elution volume, we investigated target recoveries using 0.5–4.0 mL of eluting solution. As shown in Figure 4C, recovery was highest using a

3.0 mL volume of eluting solution. Therefore, 3.0 mL was selected as the elution volume.

3.3.5 | Effects of elution time

In our extraction experiments, the target analytes were desorbed from MIL-68(Al)/MeS during vortex treatment. To determine an appropriate elution time, we investigated recoveries after elution times in the 2–16 min. range. As shown in Figure 4D, the highest recovery was obtained using an elution time of 12 min.

3.4 | Method evaluation

To further evaluate our novel extraction method, we determined the linear range of the proposed method under optimal conditions. The chromatographic peak area of extracted analyte was plotted at different input concentrations, and the results were used to establish a calibration curve (Table 1). The linear regression equations and correlation coefficients for each analyte are shown in Table 1. In the concentration range of 8–200 ng/mL, all four *p*-hydroxybenzoates demonstrated a good linear relationship ($r \geq 0.9948$).

Experiments designed to determine the quantitative limit and reproducibility were also performed under optimal conditions. For all four *p*-hydroxybenzoates tested, the LODs ($S/N = 3$) were 0.26–0.41 ng/mL. Reproducibility in this paper was assessed by measuring intra- and inter-day precision at two different concentration levels over one working day and five consecutive days, respectively. The results of these reproducibility experiments are reported in Table 1. The intra- and inter-day recovery rates for all four *p*-hydroxybenzoate samples were 91.2–98.1% and 104.0–109.7%, respectively. The corresponding RSDs for intra- and inter-day precision were 1.7–13.8 and 3.4–9.7%, respectively. The above data demonstrate that our novel method has good precision.

3.5 | Matrix effects

In the analysis of oil samples, there will be an obvious matrix, which will greatly interfere with the accuracy of the results [35]. So the following formula is used to calculate the matrix effect:

$$\text{Matrix effect} = \left[1 - \frac{A_2 - A_1}{A_0} \right] \times 100\% \quad (1)$$

A_2 , A_1 , A_0 are the peak area values of the standard solution, blank sample, and spiked sample of

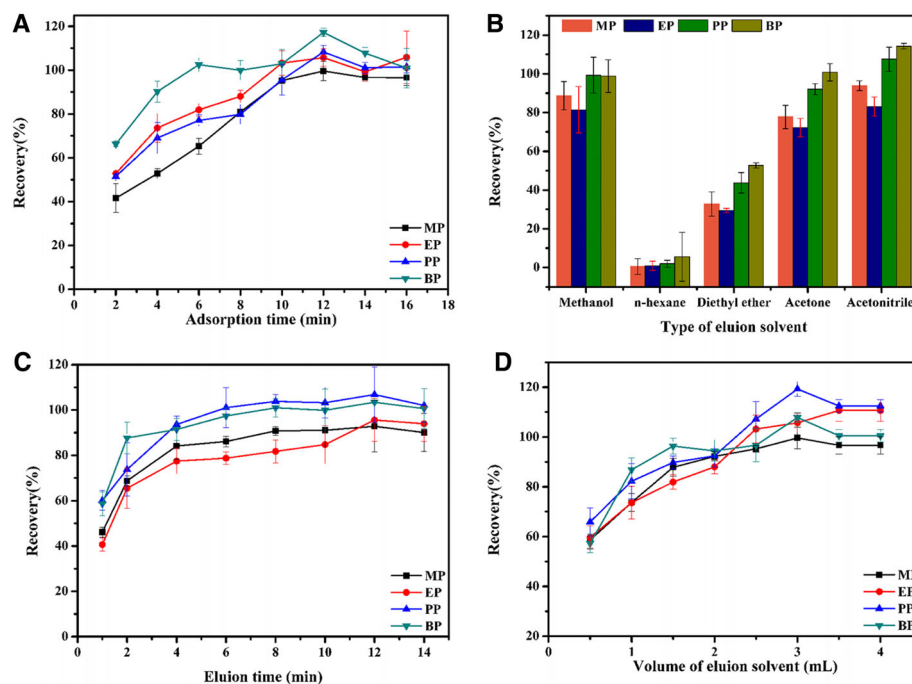


FIGURE 4 Optimization of additional experimental conditions. (A) Graph showing optimization of adsorption time. (B) Graph showing optimization of elution solvent. (C) Bar graph showing optimization of elution time. (D) Graph showing optimization of elution solvent volume

TABLE 1 Analytical performance of the present method

Analyte	Linear range (ng/mL)	Regression equation	Correlation coefficient (<i>r</i>)	Spiked (ng/mL)	Inter-day (<i>n</i> = 5)		Intra-day (<i>n</i> = 5)		Matrix (%)	LOD (ng/mL)
					Recovery (%)	RSD (%)	Recovery (%)	RSD (%)		
Methylparaben	8–200	$y = 2650.7x - 21651.4$	0.9986	40	105.1	7.2	95.3	8.6	8.4	0.26
				200	104.6	3.4	98.1	1.7		
Ethylparaben	8–200	$y = 2646.3x - 26507.9$	0.9983	40	104.6	8.2	93.1	13.8	10.0	0.29
				200	104.1	3.7	91.2	1.7		
Propylparaben	8–200	$y = 2505.0x + 43480.0$	0.9980	40	105.1	6.4	94.9	12.3	7.8	0.41
				200	108.6	4.6	94.7	2.2		
Butylparaben	8–200	$y = 2210.7x - 52058.2$	0.9948	40	104.0	9.7	95.2	12.7	11.3	0.29
				200	109.7	6.2	95.4	4.3		

p-hydroxybenzoic acid ester, respectively. The final results are shown in Table 1. The matrix effect of the four substances is less than 11.3%, so the matrix has no significant effect.

3.6 | Real sample applications

To investigate the practical applications of our novel method, three real-world samples were selected for analysis: a baby milk nourishing cream, a baby cleansing moisturizer, and an acne cream. All three samples were processed according to the steps detailed in Section 2.2. The

experiments were then performed under optimal conditions. The experimental data for these samples are reported in Table S2. The recovery values for all parabens ranged from 85.8 to 109.7% (RSDs < 9.7%). A typical chromatogram for a spiked sample is shown in Figure S5.

3.7 | Comparison of our novel method with previously reported methods

In the present study, we have proposed and optimized a novel extraction method. In Table 2, we show a comparison of the results obtained using our novel method with

TABLE 2 Comparison of the presented method with other reported methods

Matrix	Analytes	Extraction method	Extraction time (min)	Analytical technique	Recovery (%)	RSD (%)	LODs (ng/mL)	Ref.
Sunblock, hand lotion, cream, body lotion	MP, PP	SPME ^a	20	HPLC-DAD	90.9–96.1	<5.2	12–15	[36]
Water	EP, PP, BP	EME ^b	40	HPLC-DAD	80.4–103.6	<12.6	0.72–1.15	[37]
Shampoo, cream, toothpaste, wastewater	MP	DHF-LPME ^c	40	HPLC-UV	85.6–103.0	≤4.3	0.50	[38]
Rose water, Cream, Deodorant	MP, EP, PP, BP BzP	FPSE ^d	30	HPLC-UV	88.0–122.0	<5.0	0.58	[39]
Baby milk nourishing cream, Baby cleansing moisturizer, Acne cream	MP, EP, PP, BP	SPE ^e	12	HPLC-UV	91.2–109.7	≤13.8	0.26–0.41	This work

Abbreviations: BP, butylparahydroxybenzoates; EP, ethylparahydroxybenzoates; MP, methylparahydroxybenzoates; PP, propylparahydroxybenzoates.

^aSolid-phase microextraction.

^bElectro-membrane extraction.

^cDynamic hollow fiber liquid-phase microextraction.

^dFabric-phase sorptive extraction.

^eSolid-phase extraction.

previous results reported using other methods [36–39]. The extraction time required using our novel method was comparatively short. Furthermore, the use of MIL-68(Al)/MeS simplified the experimental steps, thus saving time and effort. In addition, a comparison of the data in Table 2 reveals that the extraction efficiency of our novel method was very good. Moreover, the LODs reported in our study were lower. To summarize, the novel method proposed in this study is comparatively simple and suitable for the detection of parabens in personal care products.

4 | CONCLUDING REMARKS

In the present study, PVDF was used to facilitate MIL-68(Al) functionalization of MeS to obtain a new extraction material: MIL-68(Al)/MeS. The synthesized materials were characterized by SEM, XRD, Brunauer-Emmett-Teller adsorption, and FTIR, which proved the successful synthesis and good properties of the materials. It is used in HPLC analysis, and the experimental data reveal that MIL-68(Al)/MeS demonstrates a particularly good adsorption capacity for four parabens (methylparahydroxybenzoates, ethylparahydroxybenzoates, propylparahydroxybenzoates, and butylparahydroxybenzoates). MOFs modification of MeS for extraction as reported in this paper also provides a new rationale by which MOFs can be used to modify other materials in future studies.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (Nos. 22074052 and 22004046)

and the Science and Technology Developing Foundation of Jilin Province of China (No. 20200404173YY).

CONFLICT OF INTEREST

The authors have declared no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Ying Sun  <https://orcid.org/0000-0002-6820-3184>

Xinghua Wang  <https://orcid.org/0000-0002-3769-3539>

Daqian Song  <https://orcid.org/0000-0002-5868-0649>

Qiang Fei  <https://orcid.org/0000-0001-8757-2914>

REFERENCES

- Hu K, Zhao D, Wu G, Ma J. Aromatic poly(ether ester)s derived from a naturally occurring building block nipagin and linear aliphatic α,ω -diols. *RSC Adv.* 2017;7:32989–3000.
- Pai CW, Leong D, Chen CY, Wang GS. Occurrences of pharmaceuticals and personal care products in the drinking water of Taiwan and their removal in conventional water treatment processes. *Chemosphere* 2020;256:127002.
- Goukon Y, Yasuda MT, Yasukawa H, Terasaki M. Occurrence and AhR activity of brominated parabens in the Kitakami River, North Japan. *Chemosphere* 2020;249:126152.
- Saraji M, Mirmahdieh S. Single-drop microextraction followed by in-syringe derivatization and GC-MS detection for the determination of parabens in water and cosmetic products. *J Sep Sci.* 2009;32:988–95.
- Nohynek GJ, Antignac E, Re T, Toutain H. Safety assessment of personal care products/cosmetics and their ingredients. *Toxicol Appl Pharmacol.* 2010;243:239–59.

- Boxall ABA, Rudd MA, Brooks BW, Caldwell DJ, Choi K, Hickmann S, Innes E, Ostapyk K, Staveley JP, Verslycke T, Ankley GT, Beazley KF, Belanger SE, Berninger JP, Carriquiriborde P, Coors A, DeLeo PC, Dyer SD, Ericson JF, Gagné F, Giesy JP, Gouin T, Hallstrom L, Karlsson MV, Joakim Larsson DG, Lazorchak JM, Mastrocco F, McLaughlin A, McMaster ME, Meyerhoff RD, Moore R, Parrott JL, Snape JR, Murray-Smith R, Servos MR, Sibley PK, Straub JO, Szabo ND, Topp E, Tetreault GR, Trudeau VL, Van Der Kraak G. Pharmaceuticals and personal care products in the environment: what are the big questions? *Environ Health Perspect.* 2012;120:1221–9.
- Darbre PD. Environmental oestrogens, cosmetics and breast cancer. *Best Pract Res Clin Endocrinol Metab.* 2006;20:121–43.
- Díaz-Álvarez M, Smith SP, Spivak DA, Martín-Esteban A. Preparation of molecularly imprinted polymeric fibers using a single bifunctional monomer for the solid-phase microextraction of parabens from environmental solid samples. *J Sep Sci.* 2016;39:552–8.
- Vicario A, Aragón L, Wang CC, Bertolino F, Gomez MR. A simple and highly selective molecular imprinting polymer-based methodology for propylparaben monitoring in personal care products and industrial waste waters. *J Pharm Biomed Anal.* 2018;149:225–33.
- Li JR, Sculley J, Zhou HC. Metal-organic frameworks for separations. *Chem Rev.* 2012;112:869–932.
- Chen YZ, Zhang R, Jiao L, Jiang HL. Metal-organic framework-derived porous materials for catalysis. *Coord Chem Rev.* 2018;362:1–23.
- Jiao L, Seow JYR, Skinner WS, Wang ZU, Jiang HL. Metal-organic frameworks: structures and functional applications. *Mater Today.* 2019;27:43–68.
- Li JR, Kuppler RJ, Zhou HC. Selective gas adsorption and separation in metal-organic frameworks. *Chem Soc Rev.* 2009;38:1477–504.
- Li X, Ma W, Li H, Bai Y, Liu H. Metal-organic frameworks as advanced sorbents in sample preparation for small organic analytes. *Coord Chem Rev.* 2019;397:1–13.
- Ma W, Li X, Bai Y, Liu H. Applications of metal-organic frameworks as advanced sorbents in biomacromolecules sample preparation. *TrAC Trends Anal Chem.* 2018;109:154–62.
- Chisvert A, Cárdenas S, Lucena R. Dispersive micro-solid phase extraction. *TrAC Trends Anal Chem.* 2019;112:226–33.
- Hao L, Wei J, Zheng R, Wang C, Wu Q, Wang Z. Magnetic porous carbon derived from Co-doped metal-organic frameworks for the magnetic solid-phase extraction of endocrine disrupting chemicals. *J Sep Sci.* 2017;40:3969–75.
- Qin Z, Jiang Y, Piao H, Tao S, Sun Y, Wang X, Ma P, Song D. Packed hybrids of gold nanoparticles and halloysite nanotubes for dispersive solid-phase extraction of triazine herbicides, and their subsequent determination by HPLC. *Microchim Acta.* 2019;186:489. <https://doi.org/10.1007/s00604-019-3578-3>.
- Li M: Bian C, Yang G, Qiang X. Facile fabrication of water-based and non-fluorinated superhydrophobic sponge for efficient separation of immiscible oil/water mixture and water-in-oil emulsion. *Chem Eng J.* 2019;368:350–8.
- Zhao J, Guo Q, Wang X, Xie H, Chen Y. Recycle and reusable melamine sponge coated by graphene for highly efficient oil-absorption. *Colloids Surfaces A Physicochem Eng Asp.* 2016;488:93–9.
- Song S, Yang H, Su C, Jiang Z, Lu Z. Ultrasonic-microwave assisted synthesis of stable reduced graphene oxide modified melamine foam with superhydrophobicity and high oil adsorption capacities. *Chem Eng J.* 2016;306:504–11.
- García-Valverde MT, Chatzimitakos T, Lucena R, Cárdenas S, Stalikas CD. Melamine sponge functionalized with urea-formaldehyde co-oligomers as a sorbent for the solid-phase extraction of hydrophobic analytes. *Molecules* 2595, 2018;23:<https://doi.org/10.3390/molecules23102595>.
- Qin Z, Jiang Y, Piao H, Li J, Tao S, Ma P, Wang X, Song D, Sun Y. MIL-101(Cr)/MWCNTs-functionalized melamine sponges for solid-phase extraction of triazines from corn samples, and their subsequent determination by HPLC-MS/MS. *Talanta* 2020;211:120676.
- Cui Y, He Z, Xu Y, Su Y, Ding L, Li Y. Fabrication of molecularly imprinted polymers with tunable adsorption capability based on solvent-responsive cross-linker. *Chem Eng J.* 126608, 2021;405:126608. <https://doi.org/10.1016/j.cej.2020.126608>.
- Hanikel N:Pei X, Chheda S, Lyu H, Jeong W, Sauer J, Gagliardi L, Yaghi OM. Water harvesting. *Science* 2021;459:454–9.
- Wang C, Zhou W, Liao X, Wang X, Chen Z. Covalent immobilization of metal-organic frameworks onto chemical resistant poly(ether ether ketone) jacket for stir bar extraction. *Anal Chim Acta.* 2018;1025:124–33.
- Tartaglia A, Kabir A, Ulusoy S, Sperandio E, Piccolantonio S, Ulusoy HI, Furton KG, Locatelli M. FPSE-HPLC-PDA analysis of seven paraben residues in human whole blood, plasma, and urine. *J Chromatogr B Anal Technol Biomed Life Sci.* 2019;1125:121707.
- Razavi N, Es'haghi Z. Curcumin loaded magnetic graphene oxide solid-phase extraction for the determination of parabens in toothpaste and mouthwash coupled with high performance liquid chromatography. *Microchem J.* 2019;148:616–25.
- Chen Z, Yu C, Xi J, Tang S, Bao T, Zhang J. A hybrid material prepared by controlled growth of a covalent organic framework on amino-modified MIL-68 for pipette tip solid-phase extraction of sulfonamides prior to their determination by HPLC. *Microchim Acta.* 2019;186:393. <https://doi.org/10.1007/s00604-019-3513-7>.
- Susan LY: Ismail S, Ooi BS, Mustapa H. Surface morphology of PVDF membrane and its fouling phenomenon by crude oil emulsion. *J Water Process Eng.* 2017;15:55–61.
- Tan Y, Sun Z, Meng H, Han Y, Wu J, Xu J, Xu Y, Zhang X. A new MOFs/polymer hybrid membrane: MIL-68(Al)/PVDF, fabrication and application in high-efficient removal of p-nitrophenol and methylene blue. *Sep Purif Technol.* 2019;215:217–26.
- Chen J, Deng W, Li X, Wang X, Xiao Y. Hexafluoroisopropanol/Brij-35 based supramolecular solvent for liquid-phase microextraction of parabens in different matrix samples. *J Chromatogr A.* 2019;1591:33–43.
- Zhao X, Liu D, Huang H, Zhang W, Yang Q, Zhong C. The stability and defluoridation performance of MOFs in fluoride solutions. *Micropor Mesopor Mater.* 2014;185:72–8.
- Ariffin MM, Sohaimi NM, Yih BS, Saleh NM. Magnetite nanoparticles coated with surfactant Sylgard 309 and its application as an adsorbent for paraben extraction from pharmaceutical and water samples. *Anal Methods.* 2019;11:4126–36.
- Jiang Y, Qin Z, Song X, Piao H, Li J, Wang X, Song D, Ma P, Sun Y. Facile preparation of metal-organic framework-based laboratory semi-automatic micro-extraction syringe packed column

- for analysis of parabens in vegetable oil samples. *Microchem J.* 2020;158:105200.
36. Fei T, Li H, Ding M, Ito M, Lin JM. Determination of parabens in cosmetic products by solid-phase microextraction of poly(ethylene glycol) diacrylate thin film on fibers and ultra-high-speed liquid chromatography with diode array detector. *J Sep Sci.* 2011;34:1599–606.
37. Villar-Navarro M, Moreno-Carballo MDC, Fernández-Torres R, Callejón-Mochón M, Bello-López MÁ. Electromembrane extraction for the determination of parabens in water samples. *Anal Bioanal Chem.* 2016;408:1615–21.
38. Esrafil A, Yamini Y, Ghambarian M, Moradi M. Analysis of paraben preservatives in cosmetic samples: comparison of three different dynamic hollow fiber liquid-phase microextraction methods. *Chromatographia* 2014;77:317–27.
39. Kaur R, Heena Kaur R, Grover A, Rani S, Malik AK, Kabir A, Furton KG. Trace determination of parabens in cosmetics and personal care products using fabric-phase sorptive extraction

and high-performance liquid chromatography with UV detection. *J Sep Sci.* 2020;43:2626–35.

SUPPORTING INFORMATION

Additional supporting information may be found in the online version of the article at the publisher's website.

How to cite this article: Li J, Jiang Y, Sun Y, Wang X, Ma P, Song D, Fei Q. Extraction of parabens by melamine sponge with determination by high-performance liquid chromatography. *J Sep Sci.* 2022;45:697–705.

<https://doi.org/10.1002/jssc.202100817>