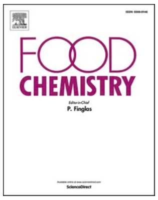
Food Chemistry 445 (2024) 138802

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem



FOOD CHEMISTRY

Covalent organic framework reinforced hollow fiber bar for extraction and detection of bisphenols from beverages

Shu-Ting Cheng, Jin-Yu Qiao, Hong-Ming Zhang, Xiao-Fang Shen, Yue-Hong Pang [*]

State Key Laboratory of Food Science and Resources, School of Food Science and Technology, Jiangnan University, Wuxi 214122, China

ARTICLE INFO

Keywords:
Covalent organic framework
Hollow fiber bar
Extraction efficiency
Bisphenols
Beverages

ABSTRACT

Bisphenols (BPs) can migrate from packaging materials into foods, resulting in potentially harmful residues. For example, accumulation of BPs is associated with endocrine disorders. Owing to matrix effects, development of an effective and eco-friendly sample pretreatment would be helpful for BPs detection in beverages packed in plastic containers. In this work, an extraction bar, composed of hollow fiber (HF) functionalized with covalent organic frameworks (COF@Tp-NDA) and 1-ocanol, was prepared for extraction of five BPs simultaneously. The synergistic effect of COF@Tp-NDA and 1-octanol improved the extraction efficiency of BPs from milk-based beverage, juice, and tea beverage. Under optimal conditions, limits of detection ranged from 0.10 to 2.00 ng mL^{-1} ($R^2 \geq 0.9974$) and recoveries ranged from 70.1 % to 106.8 %. This method has the potential to enrich BPs, supporting their accurate determination in complex beverages.

1. Introduction

Bisphenols (BPs) are a group of chemicals containing two phenolic functional groups connected by bridging carbon (Vaghela, Kulkarni, Karve, & Zinjarde, 2022). They can simulate the binding of estrogen to its receptor, thereby disrupting the endocrine system and leading to the occurrence of metabolic diseases (Gallo et al., 2017; Grimaldi, Boulahtouf, Toporova, & Balaguer, 2019). Among them, BPA is a common compound used in the production of polycarbonate plastics, epoxy resins, food and beverage packaging. It can migrate into the packaging contents and subsequently be ingested by the human body during the process of food production, storage and transportation (Almeida, Raposo, Almeida-González, & Carrascosa, 2018; Ma et al., 2019; Zhang et al., 2022). With the increased exposure, BPA and their metabolites accumulate in the body, thus has a prolonged impact on human health (Xu et al., 2022). Due to the increasing regulation and restriction on the manufactory and usage of BPA, various BPA analogues have been developed and used in the food industry as substitutes for BPA (Catenza, Farooq, Shubear, & Donkor, 2021). Nevertheless, studies have revealed that the toxicity of these BPA analogues is comparable to or even exceeds the toxicity of BPA itself (Chen et al., 2016; Hercog et al., 2019; Liu et al., 2021). Therefore, it is critical to develop a sensitive method to detect BPs in food and beverage packaging (Dong, Tan, Chen, & Liu, 2015).

Various analytical techniques have been developed for the determination of BPs in food samples, including high performance liquid chromatography detection (HPLC) (Xiong et al., 2018; Han et al., 2021), gas chromatography detection (Owczarek et al., 2022), capillary electrophoresis (Zhang, Zhu, Huang, Sun, & Lee, 2015) and electrochemical method (Jemmeli, Marcoccio, Moscone, Dridi, & Arduini, 2020). HPLC offers high selectivity and sensitivity, which is conducive to the efficient separation and detection of BPs. In complex matrix food samples, BPs usually exist at trace levels, hence enrichment extraction is a key point in BPs detection. To achieve this, several extraction methods have been employed for BPs enrichment, including dispersive liquid–liquid microextraction (DLLME) (Qu et al., 2019), solid-phase extraction (SPE) (Li et al., 2018b), dispersive solid-phase extraction (d-SPE) (Liu et al., 2022a), and magnetic solid-phase extraction (MSPE) (Pang, Yue, Huang, Yang, & Shen, 2020). While traditional extraction methods require the additional centrifugation and magnet adsorption to separate the extraction phase or extractant, this process is not only time-consuming and labor-intensive, but also may result in loss of the adsorbent during the operation (Deng, Li, Jiang, Lin, & Zhao, 2019; Kannouma, Hammad, Kamal, & Mansour, 2022; Ocaña-Rios, de Jesús Olmos-Espejel, & Donkor, 2022). Moreover, the unselective absorption of other endogenous compounds in the sample matrices may cause the saturation and breakthrough of the adsorbent, ultimately affecting the detection of the analyte (Xia, Du, Xiao, & Li, 2019). Therefore, it is of great importance

---

* Corresponding author.
E-mail address: yhpang@jiangnan.edu.cn (Y.-H. Pang).

https://doi.org/10.1016/j.foodchem.2024.138802
Received 28 November 2023; Received in revised form 14 February 2024; Accepted 16 February 2024

to develop a convenient and efficient pretreatment to eliminate the matrix interference.

Hollow fiber (HF) has a micro-hollow cylinder structure that can accommodate the desired extractant (Li et al., 2018a). The surface of cylinder is constructed with cross-fiber micropores, whose wall holes can prevent the penetration of macromolecules and particles during enrichment and extraction. Therefore, the HF supported extraction system has a function of sample purification (Li, Xue, Fu, Ma, & Feng, 2022; Yamini, Faraji, & Ghambarian, 2015). The hollow cylinder shape of the HF provides a holding site for the liquid extractant, preventing the dispersion in the enrichment and extraction. The functional molecules can be modified on HF surface to further improve the extraction efficiency.

Covalent organic frameworks (COFs) are a class of porous crystalline organic materials with potential extraction ability owing to the large specific surface area, porosity, and robust stability (Chang et al., 2019; Côté et al., 2005; Karak, Dey, & Banerjee, 2022; Segura, Royuela, & Mar Ramos, 2019; Song, Sun, Aguila, & Ma, 2019). When loaded on HF, COFs effectively prevent dispersion in solution, facilitating the separation and collection. Liu et al. improved the extraction efficiency of benzophenones by modifying COF-V on HF (achieving enrichment factors 49–102) (Liu et al., 2022b). Moreover, due to the lipophilicity, BPs exhibit a high affinity for dissolving in organic solvents, following the principle of similar solubility (Alampanos, Kabir, Furton, Panderi, & Samanidou, 2022). Nowadays, there are few reports on the combined extraction of COF and organic solvents with HF.

Herein, three different COFs were synthesized by solvent-thermal method to assess the extraction ability of BPs. COF-1,3,5-trimethylphloroglucinol-1,5-diaminonaphthalene (COF@Tp-NDA) was chosen for further modification onto HF to prepare HF@COF@Tp-NDA extraction bar. For the extraction of five bisphenols (BPA, BPB, BPAF, BPF, BPZ), 1-octanol was injected into the HF@COF@Tp-NDA, coupling with HPLC for quantitative analysis and detection. The reproducibility and feasibility of HF@COF@Tp-NDA were further evaluated. Finally, the developed method was applied to the enrichment and detection of BPs in beverages to verify the accuracy.

2. Materials and methods

2.1. *Reagent and materials*

1,3,5-trimethylphloroglucinol (Tp), 1,5-diaminonaphthalene (NDA), benzidine (BD), 2,6-diaminoanthraquinone (DQ), 1-octanol, a series of BPs (BPA, BPB, BPZ, BPF, BPAF), chromatographic grade methanol, ethanol and acetonitrile were purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Glacial acetic acid, acetone and 1,4-dioxane were received from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Polypropylene HF membrane was acquired from Membrana GmbH (Wuppertal, Germany).

2.2. *Apparatus*

The SU8100 scanning electron microscope (SEM, Hitachi, Tokyo, Japan) was used to characterize the coating of fiber. The functional groups were characterized by NEXUS 870 Fourier transform infrared (FT-IR) spectra (ThermoFisher Scientific, Waltham, USA). D8 Advance X-ray diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) was conducted to characterize the crystal phase. Nitrogen adsorption–desorption experiments were performed with automatic specific surface and porosity analyzer (Micromeritics Instrument, Norcross, USA).

2.3. *Preparation of COFs and extraction of BPs*

Three different COFs were synthesized by solvothermal method (Fig. S1). (A) Tp-NDA: Tp (63 mg) and NDA (71 mg) were dissolved in 1, 4-dioxane solution (3 mL), then mixed thoroughly by ultrasonication and the resultant solution was added into acetic acid solution (6 mol/L, 0.6 mL). The mixture was under ultrasonication for 30 min and placed in an oven at 120 ℃ for 3 days to allow synthesis reaction to occur. The obtained material after the reaction was cleaned with 1, 4-dioxane and tetrahydrofuran, sequentially and dried at 60 ℃ under vacuum condition. (B) TPBD: Tp (63 mg) and BD (83 mg) were dissolved in mesitylene and 1, 4-dioxane (3 mL), respectively. The mixed solution was added to acetic acid solution (6 mol/L, 0.5 mL) and mixed under ultrasonication for 30 min and reaction was carried out at 120 °C for 3 days. The products were cleaned with tetrahydrofuran, N, *N*-dimethylformamide and acetone, and dried at 60 ℃ under vacuum condition. (C) DQTP: DQ (68 mg) and Tp (40 mg) were dissolved in 1, 4-dioxane (1 mL) respectively. After mixing the two solutions, acetic acid (6 mol/L, 0.1 mL) was added to the mixture, and then further mixed by ultrasonication for 30 min, and the reaction was carried out at 120 ℃ for 2 days. The reaction product was washed with deionized water, ethanol and acetone and dried under vacuum before use.

The obtained three COFs were ground into powder and used for extraction of BPs. 5 mg COFs were dispersed into 10 mL BPs solution. After the ultrasonic extraction (10 min), COFs were centrifuged for 5 min (10,000 r/min, r = 10 cm), then supernatant was discharged to collect COFs. Methanol was used for analyte desorption with the aid of ultrasonication (5 min) and subsequently centrifuged. The collected supernatant was analyzed and detected by HPLC with fluorescence detector (HPLC-FLD) after through 0.22 μm nylon filtration membrane.

2.4. *Fabrication of COFs modified hollow fiber extraction bar*

HF was cut into small segments of 2 cm in length each, ultrasonically soaked in methanol for 10 min, and dried at 60 ℃. 50 mg COFs was ultrasonically dispersed in 20 mL methanol solution to obtain suspension. The cleaned HF was then put in the suspension with ultrasonic treatment for 1 h. COFs were fixed and modified on the cross micropores of HF under the ultrasonication and capillary. The residual COFs in suspension could be reused after centrifugal filtration and drying. After that, HF was removed and the unbonded COFs was cleaned with methanol. COFs functionalized HF (HF@COFs) was obtained when the washing solution was colorless. Finally, HF@COFs was used to prepare the extraction bar. 1-octanol (10 μL) was firmly sealed and fixed in HF@COFs to avoid unnecessary leakage loss during use.

2.5. *High performance liquid chromatography analysis conditions*

The chromatographic analysis was performed using a Waters 1525 HPLC system equipped with a 2475 fluorescence detector. The separation and quantification were performed on a Waters C18 column (250 × 4.6 mm, 5 μm). The mobile phase was a mixture of acetonitrile (A) and water (B), and the gradient elution program was as follows: 0 ~ 5 min, 60 % A; 5 ~ 8 min, 60–70 % A; 8 ~ 10 min, 70–60 % A; 10 ~ 15 min, 60 % A. The excitation wavelength was 227 nm, and emission wavelength was 319 nm. The column temperature was set 25 ℃, flow rate was 0.8 mL $\min^{-1}$ and the injection volume was 20 μL. The HPLC method for the determination of BPs was validated for linearity, recovery, precision, limit of detection (LOD) and limit of quantification (LOQ) according to AOAC (2012) and Chinese Pharmacopoeia Commission (2020). All experiments were performed with three sample replicates (n = 3).

2.6. *Pretreatment of samples*

The three types of plastic-packaged beverages including tea beverage, juice and milk-based beverage were purchased from local supermarkets (Wuxi, China). Due to its large amounts of macromolecular substances such as proteins, milk-based beverage required a series of treatments prior to the HF@COF@Tp-NDA extraction. 10 mL of milk-based beverage was mixed with the same volume of acetonitrile for 5

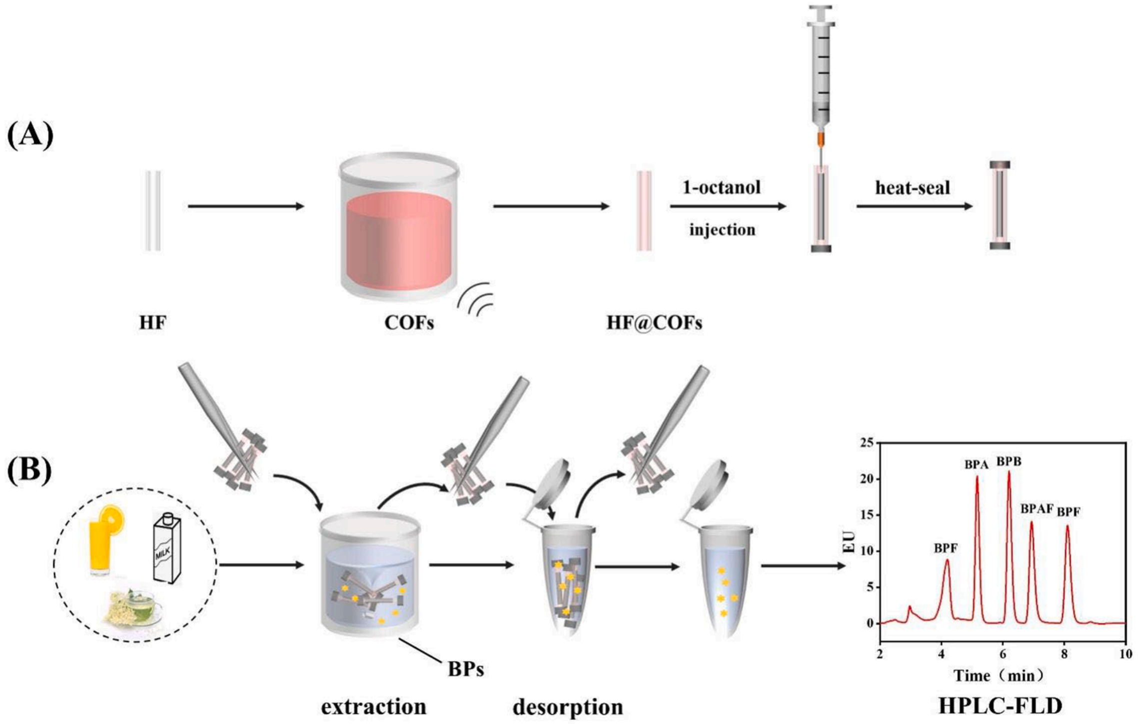


Fig. 1. Schematic diagram of (A) COF@Tp-NDA modified hollow fiber extraction bar; (B) HF@COF@Tp-NDA extraction bars for enrichment and determination of BPs in beverages.

min by vortexing, following centrifugation for 10 min (8000 r/min, r = 10 cm) at 4 ℃. The supernatant was collected and blew down dryness with nitrogen stream at 40 ℃ and redissolved with 10 mL deionized water for subsequent enrichment and extraction experiments. Tea beverage and juice were filtered through a 0.22 μm membrane filter before extraction process. The beverages samples (n = 3 for each beverage) were spiked with the specific volume of BPs standard solution. Then, the desorption liquid obtained from the extraction process was passed through the membrane to HPLC-FLD for analysis.

3. Results and discussion

3.1. *The design of HF@COF@Tp-NDA extraction bar for BPs extraction*

To study the extraction efficiency of BPs by COFs, three different synthetic monomer, Tp-NDA, TPBD, and DQTP were selected for comparison with the extraction of BPs. As shown in Fig. S2A and B, COF@Tp-NDA showed the highest extraction efficiency of BPs, which can be attributed to the narrower pore size of COF@Tp-NDA (17 Å) compared to COF@TPBD (23 Å) and COF@DQTP (32 Å). The molecular diameter of BPs ranged from 9.1 to 10.5 Å (Fig. S2C), indicating the larger pore size has a less effect on the pore size of BPs and possess weaker binding force. Moreover, studies have shown that the larger pore size of COFs is unfavorable for the extraction of organic compounds (Zhang et al., 2020). Thus, COF@Tp-NDA was chosen to modify hollow fiber for extraction of BPs.

Under the synergic action betwwen COF@Tp-NDA and 1-octanol, BPs were adsorted onto the extraction bar from the aqueous solution to achieve enrichment. The extraction bar can be directly removed from the matrix after the extraction, eliminating the need for centrifugation or magnetic separation, thereby saving operation time. The consumption amount of liquid-phase and solid-phase extractants was less and the HF@COF@Tp-NDA extraction bar was portable. Finally, HPLC-FLD was used for quantitative detection (Fig. 1).

3.2. *Characterization of the COF@Tp-NDA and HF@COF@Tp-NDA*

The microscopic morphology of COF@Tp-NDA was observed by SEM, the synthesized COF@Tp-NDA appeared as in red powder with a loose porous structure (Fig. 2A). In Fig. 2B, the characteristic peaks of C—N and C═C appeared at 1252 cm^{-1} and 1583 cm^{-1}, indicating the presence of COF@Tp-NDA, while the disappear of N—H at 3300–3100 cm^{-1}, decay of C═O at 1641 cm^{-1} both support the successful synthesis. X-ray diffraction (XRD) was used to characterize the crystal structure of synthesized COF@Tp-NDA (Fig. 2C). Three peaks, at 7.21°, 12.0°, and a broad peak at about 26.1° observed were consistent with previous report (Das et al., 2018). The particle size of COF@Tp-NDA was measured at 406 nm (Fig. 2D) by using the nanoparticle size analyzer, which allows its modification in the cross-pore channel of HF. The specific surface area and pore size distribution of COF@Tp-NDA were calculated by BET model as 158.17 $m^2\ g^{-1}$ and of 1.7 nm, respectively (Fig. 2E and F).

In addition, the appearance of HF pre- and post-modification was characterized by SEM (Fig. 3A). Porous structures with various sizes were found on the surface of HF, which provided suitable sites for the modification of COF@Tp-NDA. In the subsequent enrichment and extraction of BPs, the porous structure of HF enables the separation of macromolecules from the targets in the samples, minimizing interference from the contamination of extractants in HF. Visual inspection of the HF before and after modification (Fig. 3B) revealed a distinct change in appearance. The HF exhibited a milky white hue, while the surface of HF@COF@Tp-NDA exhibited a prominent red coloration, which was similar to the color of COF@Tp-NDA powder. This observation indicated the successful modification of COF@Tp-NDA onto the HF. The EDX characterization showed a large amount of oxygen and carbon distribution upon the surface of HF@COF@Tp-NDA (Fig. 3C and D), which further confirmed the uniform distribution of COF@Tp-NDA on HF.

To investigate the stability of COF@Tp-NDA, it was respectively immersed in water, acidic and alkaline solutions for 1 day, FT-IR was performed to characterize its chemical bond structure. The spectrum (Fig. 3E) showed infrared absorption characteristic peaks of C═O and C—N remained unchanged, indicating that COF@Tp-NDA exhibits high

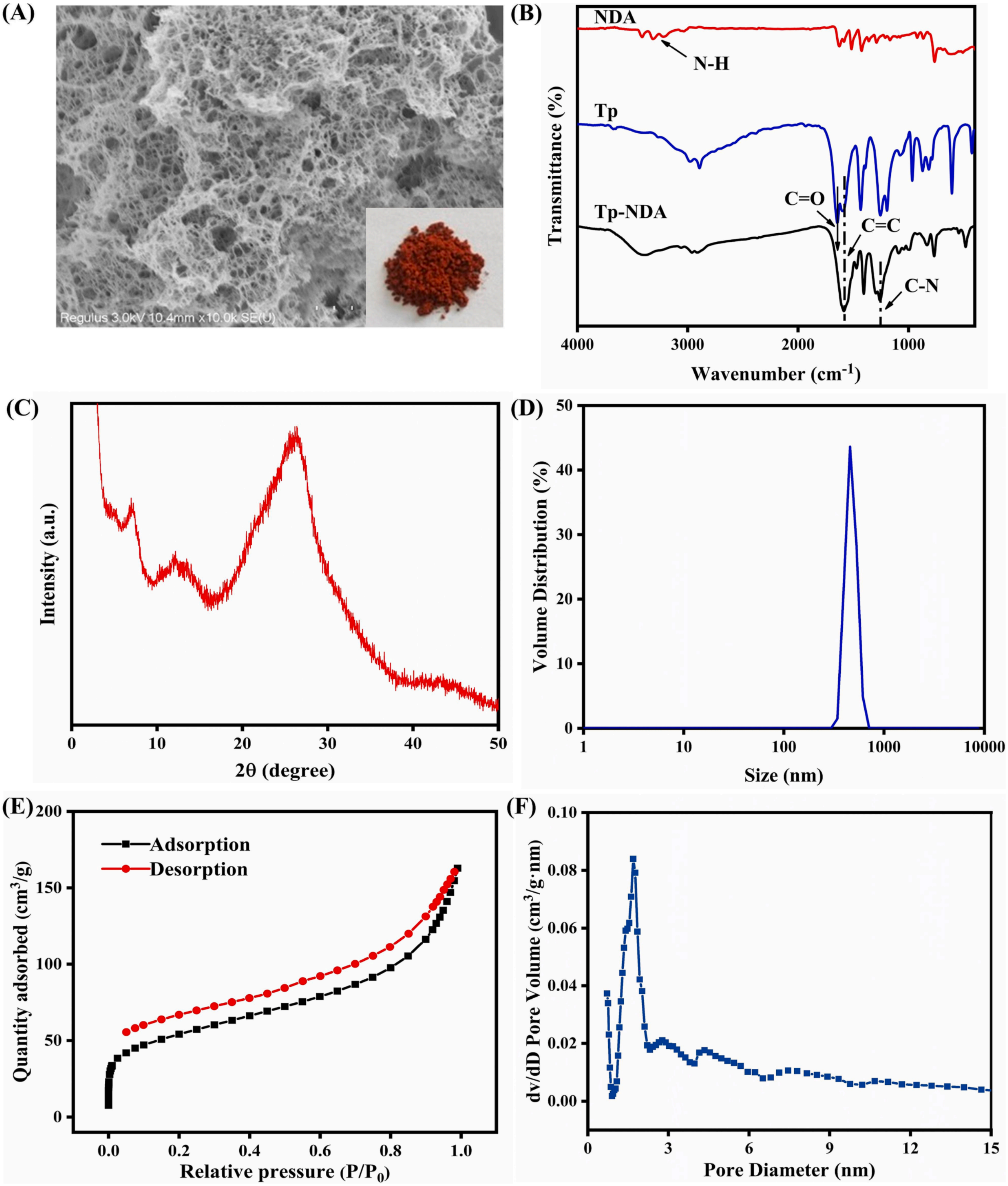


Fig. 2. (A) SEM image of COF@Tp-NDA (Inset: Photograph of COF@Tp-NDA); (B) FT-IR spectra of NDA, Tp and COF@Tp-NDA; (C) XRD image of COF@Tp-NDA; (D) Particle size distribution of COF@Tp-NDA; (E) N_2 adsorption–desorption isotherms of COF@Tp-NDA; (F) Pore size distribution of COF@Tp-NDA.

acid and alkali stability. Moreover, its organic resistance was characterized by observing its infrared absorption peak changes for immersion in 7 organic reagents (methanol, ethanol, acetonitrile, acetone, tetrahydrofuran, 1, 4-dioxane and 1-octanol) for 1 day (Fig. 3F). Notably, the FT-IR spectrum of COF@Tp-NDA maintained its integrity with distinct characteristic peaks, indicating that COF@Tp-NDA has good stability in these organic solvents and it can withstand even more severe experimental conditions.

3.3. *Comparison of extraction capacity under different HF conditions*

To explore the role of HF in extraction, BPs extraction with and without HF were compared in Fig. 4A and B. The results showed the peak area obtained by BPs extraction with 1-octanol encapsulated by HF was 1.82–2.20 times larger than that of 1-octanol alone. This suggests that 1-octanol is effectively immobilized within HF, enabling its complete recovery and simplified operation during the separation process. Compared with centrifugal separation, the loss of 1-octanol is less. In

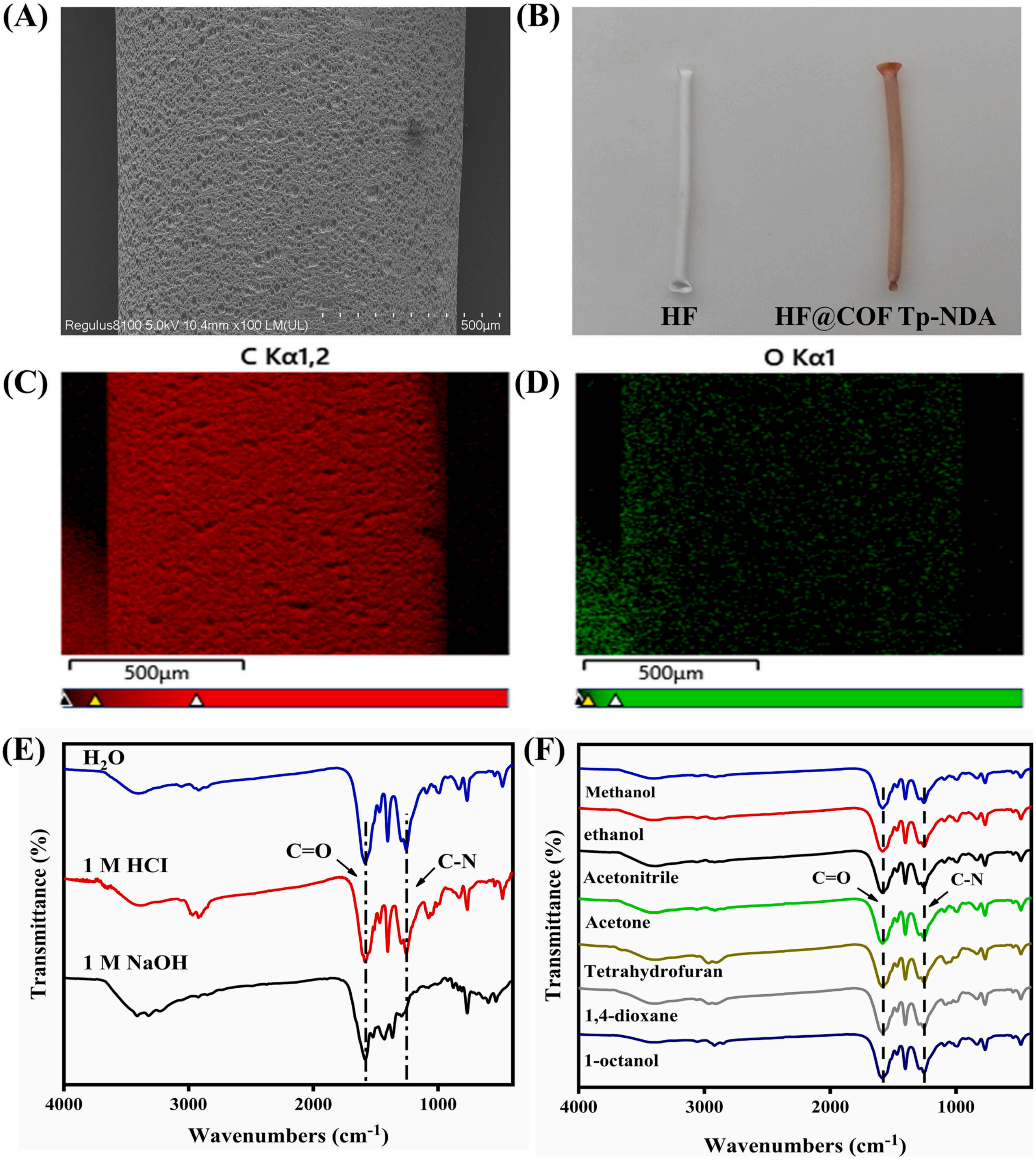


Fig. 3. (A) SEM image of HF; (B) Comparison photograph before and after HF modification; EDX elemental mapping of (C) carbon and (D) oxygen of HF@COF@Tp-NDA; FT-IR spectra of COF@Tp-NDA soaked in (E) acid, alkali, water and (F) organic solvent for one day.

addition, the extraction of BPs under four conditions were investigated in Fig. 4C and D. The peak areas of BPs extraction by HF@COF@Tp-NDA, HF + 1-octanol and HF@COF@Tp-NDA + 1-octanol were 1.31–1.57 times, 6.02–8.95 times, 6.96–10.82 times larger than that of HF, respectively. Among them, HF@COF@Tp-NDA + 1-octanol achieved the largest peak area. The combination of COF@Tp-NDA and 1-octanol on HF modification had a positive effect on the extraction of BPs, indicating that the synergistic effect of 1-octanol and COF@Tp-NDA has great potential for enrichment and extraction of BPs. BPs possess two benzene rings with a molecular diameter of 9.1–10.5 Å, which allows for adsorption by COF@Tp-NDA's large π-conjugated system with a pore size of 17 Å through π-π interactions and pore size effects. Moreover, due to the lipid solubility property of BPs, its logK_{ow} values ranged from 3.06 to 5.00 (>1), and the partition ratio of BPs in the organic phase was larger than that in the aqueous phase (Table S1). This facilitates the separation of BPs from the aqueous solution and its migration into the 1-octanol solution. Therefore, the synergistic effect of 1-octanol and COF@Tp-NDA on the HF@COF@Tp-NDA extraction bar effectively enhances the enrichment of BPs.

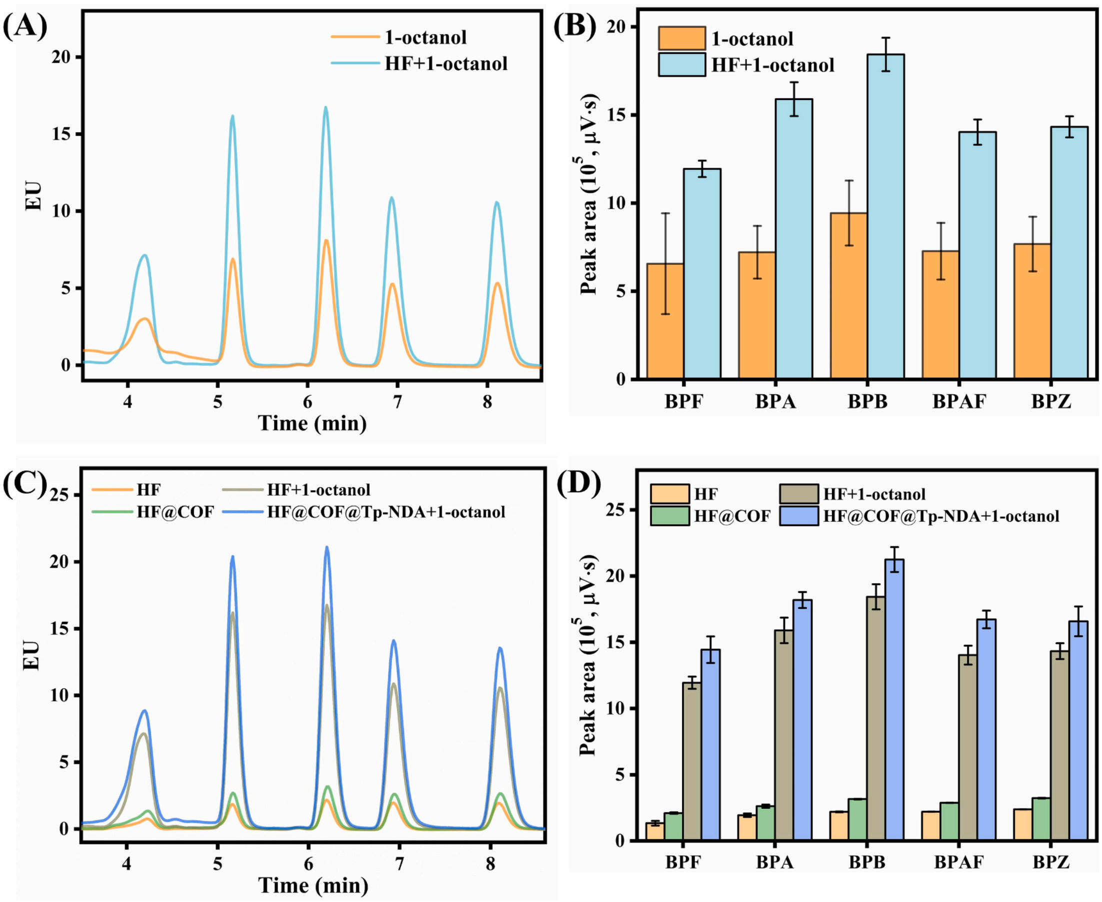


Fig. 4. Comparison of extraction effects of 1-octanol and HF + 1-octanol (A: chromatogram; from left to right: BPF, BPA, BPB, BPAF, BPZ. B: peak areas map); Comparison of extraction effects of HF, HF@COF@Tp-NDA, HF + 1-octanol and HF@COF@Tp-NDA + 1-octanol (C: chromatogram; D: peak areas map).

3.4. Optimization of experimental parameters

To ensure sufficient adsorption capacity for BPs, it is essential to utilize an appropriate amount of HF@COF@Tp-NDA extraction bar. The effect of extraction bars on BPs extraction was exhibited in Fig. 5A. The peak area of BPs exhibited a gradual growth trend as the number of extraction bars increased from 1 to 4, reaching a plateau as the number of bars further increased. It indicated that four HF@COF@Tp-NDA extraction bars are adequate for complete extraction of BPs, and adding additional bars does not facilitate subsequent desorption. Therefore, four HF@COF@Tp-NDA extraction bars were selected for the following experiments.

To expedite the extraction process, it is important to enhance the mass transfer rate of BPs by stirring under suitable conditions. HF@COF@Tp-NDA extraction bars could be rotated in BPs aqueous solution, which not only increase contact area with the extraction solution but also improve the extraction efficiency of BPs. The influence of different stirring rates on BPs extraction was further investigated in Fig. 5B. When the speed was 800 rpm, HF@COF@Tp-NDA extraction bar barely rotated but remained on the surface of the solution. As the speed increased, the vortex generated by the magnetic rotor caused the HF@COF@Tp-NDA extraction bar to rotate below the liquid level, thereby increasing its contact area with the solution. The results showed that the peak area of BPs increase with the increase of stirring rate until it stabilized at 1400 rpm. Therefore, 1400 rpm was selected for the subsequent speed.

The extraction time is crucial for the accuracy of BPs enrichment detection. To investigate its impact, the influence of different extraction times on the extraction efficiency of BPs was shown in Fig. 5C. Within 5–30 min, the peak area of BPs gradually increased with the extension of extraction time, indicating that some BPs remained in the aqueous solution during this period. After 30 min, the peak area of BPs stabilized, demonstrating that the extraction of BPs using the HF@COF@Tp-NDA extraction bar was complete. Therefore, 30 min was the following extraction time.

The selection of desorption solvent is very important for the accurate evaluation and detection of BPs. To compare their desorption performance, three solvents (methanol, acetonitrile, and ethanol) with good solubility for BPs were evaluated in Fig. 5D. The results showed that methanol has a better recovery compared to acetonitrile and ethanol. Therefore, methanol was chosen as the preferred desorption solvent.

The desorption volume should be sufficient to completely cover the HF@COF@Tp-NDA extraction bar and ensure thorough contact with the desorption solution, thereby guaranteeing the complete desorption of BPs from the HF@COF@Tp-NDA extraction bar. Therefore, the effect of desorption volume (0.5–2 mL) on BPs desorption was investigated in Fig. 5E. The results indicated that the recovery rate of BPs was better in 1 mL methanol solution for desorption. Furthermore, analysis of desorption times revealed that the highest recovery rate of BPs occurred when the extraction bar was desorbed twice in 0.5 mL of methanol solution (3 min each time). Therefore, a desorption volume of 0.5 mL × 2 was selected for subsequent experiments.

The desorption time plays a significant role in the recovery of BPs, and it determines whether BPs can be fully desorbed from the extraction bar into the solution. Fig. 5F showed that the recovery rate of BPs increased over the desorption time range from 2 to 6 min, reaching a peak at 6 min, indicating that BPs are completely desorbed from the HF@COF@Tp-NDA extraction bar at this time. However, with the

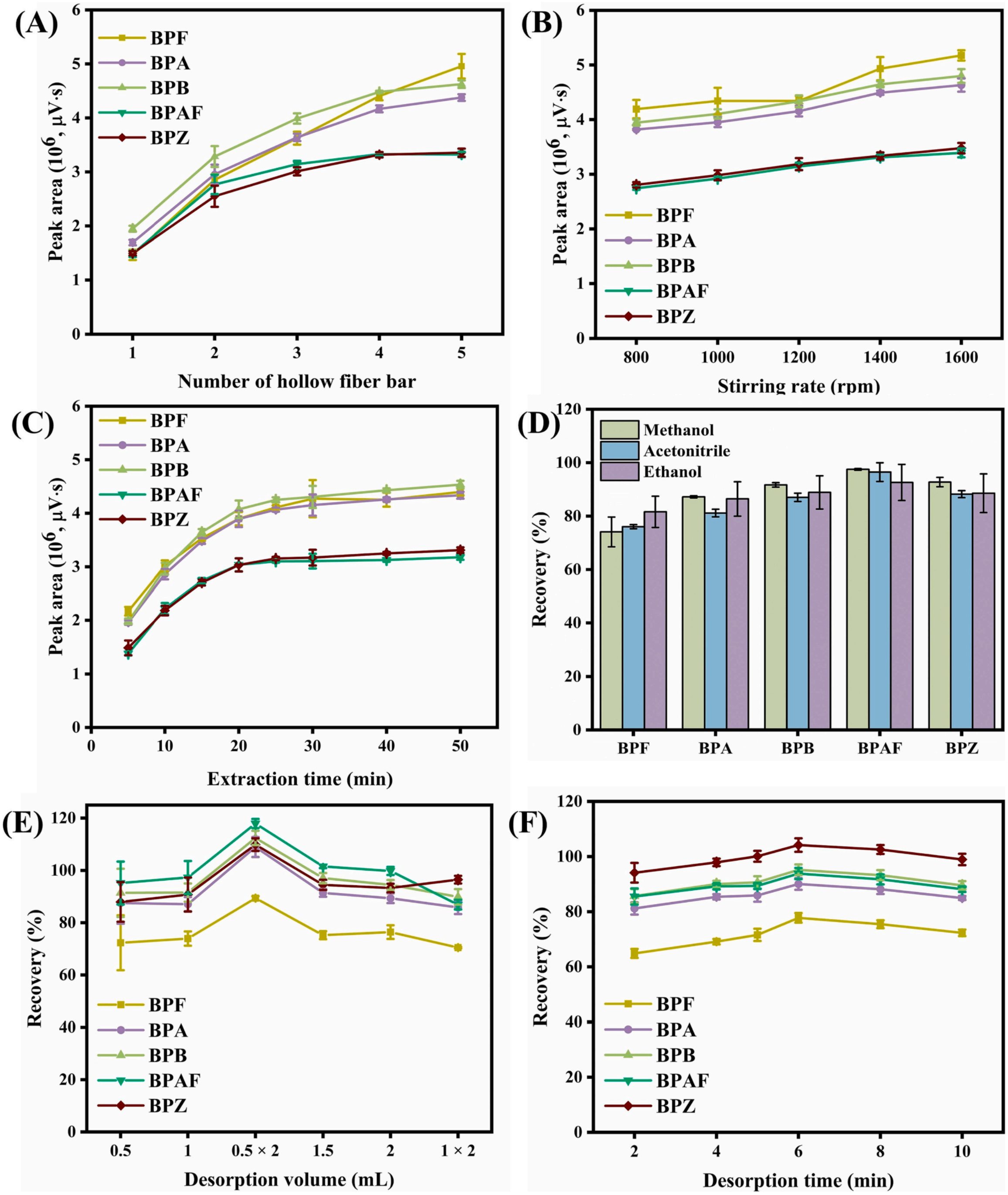


Fig. 5. Optimization of extraction and desorption conditions for 200 ng mL^{-1} bisphenols: (A) number of hollow fiber bar; (B) stirring rate; (C) extraction time; (D) desorption solvent; (E) desorption volume; (F) desorption time.

Table 1
Analytical performance of the developed method for determination of BPs.

BPs	R^2	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	Range (ng mL^{-1})	Enrichment factor	RSD (%)		
						Intra-day (n = 6)	Inter-day (n = 3)	Inter-batch (n = 3)
BPF	0.9990	0.20	0.50	5–1000	84	3.10	8.33	3.40
BPA	0.9995	0.10	0.40	5–1000	93	3.03	5.42	4.61
BPB	0.9992	0.80	2.00	5–1000	110	3.13	5.56	4.39
BPAF	0.9993	2.00	5.00	5–1000	126	2.77	5.05	3.85
BPZ	0.9974	2.00	5.00	5–1000	122	2.85	4.61	4.27

further extension of the desorption time, the recovery of BPs showed a slight decrease, possibly due to BPs redissolving in the HF@COF@Tp-NDA extraction bar. Hence, 6 min was selected as the optimal desorption time.

3.5. Method validation

The analytical performance parameters including linear range, LODs, LOQs, correlation coefficient (R^2), and relative standard deviations (RSDs) were evaluated under the optimized experimental conditions. Table 1 shows that the five BPs have good linearity in the concentration range of 5–1000 ng mL^{-1} (Fig. S3), with $R^2 \geq 0.9974$. The LODs and LOQs were 0.10–2.00 ng mL^{-1} and 0.40–5.00 ng mL^{-1}, respectively. The enrichment factors of five BPs were 84, 93, 110, 126 and 122 respectively, indicating the developed method obtained an effective enrichment. To assess reproducibility and stability, RSDs of intra-day, inter-day, and inter-batch were measured. The intra-day precision was determined with the prepared extraction bar to perform six replicate extractions of BPs solution on one day ($n = 6$), with intra-day RSDs ranging from 2.77 % to 3.13 %. The inter-day repeatability was evaluated on same extraction bars over three consecutive days ($n = 3$) and the inter-day RSDs varied from 4.61 % to 8.33 %. The inter-batch experiment was performed with three prepared HF@COF@Tp-NDA extraction bars under the same experimental conditions ($n = 3$), and the inter-batch RSDs were in the range of 3.40 %-4.61 %. These indicated that the prepared HF@COF@Tp-NDA extraction bar has good reproducibility and stability. The greenness of the developed method was evaluated using Analytical Eco-Scale (AES) metric systems, and the AES score was exhibited in Table S4. The AES score was calculated as 81, indicating that the developed method could be considered as excellent green analysis (>75).

3.6. Comparison with other reported methods

Compared with other extraction and detection methods of BPs (Table S2), the developed method had the advantages of small amount of organic solvent, wide linear range, simple operation and good portability, and the LODs was equivalent to other methods, which could meet the detection of BPs in actual samples. The developed method eliminates the need for external auxiliary devices such as centrifuge or magnet to separate the HF@COF@Tp-NDA extraction bar from the matrix, which saved the operation time. Moreover, HF@COF@Tp-NDA could encapsulate the extractant (1-octanol) inside. Due to the cross-porous structure of the HF surface, it could effectively isolate the macromolecular substances in complex matrices, preserving the extractant and ensuring accurate detection. The approach is conducive to the extraction and detection of complex matrix foods.

3.7. Application of beverages samples

To assess the practical application of the developed method, tea beverage, juice and milk-based beverage were used as real samples for enrichment and detection of BPs, and the results are detailed in Table S3 and Fig. S4. Only BPB was detected in tea beverage at a concentration of 14.57 ng mL^{-1}, while the other four BPs were not detected in the other three beverages, indicating that BPA analogues are prevalent in our daily life. To further validate the accuracy of the developed method, recovery experiments were conducted on these beverages at spiked concentrations level of 20 ng mL^{-1}, 50 ng mL^{-1} and 100 ng mL^{-1}. The recovery rates of tea beverage, juice and milk-based beverage were 86.6 %–104.3 %, 70.1 %-106.8 %, and 71.7 %–102.9 % respectively, with RSDs less than 9.6 %. These results demonstrated the developed method is accurate and feasible for the extraction and detection of BPs in beverages.

4. Conclusion

In this work, HF@COF@Tp-NDA extraction bar was prepared for hollow-fiber stir-bar liquid-phase microextraction (HF-SBLPME) coupling with HPLC for determination of trace levels of 5 BPs (BPA, BPB, BPF, BPAF and BPZ). HF@COF@Tp-NDA extraction bar can be quickly separated from the matrix, the consumption amount of liquid-phase and solid-phase extractants is less, offering advantages in terms of simple operation and green economy. In addition, the prepared COF@Tp-NDA had good chemical stability in acid solution, alkali solution and organic solution, it can withstand even more severe experimental conditions. The developed method was further applied to beverages samples, achieving recovery rates ranging from 70.1 % to 106.8 % with RSDs values less than 9.6 %. This HF-SBLPME approach has great potential for enrichment and detection of bisphenols in complex matrix foods. Moreover, HF@COF@Tp-NDA extraction bar has convenient portability owing to the small size, making it potential for batch application.

CRediT authorship contribution statement

Shu-Ting Cheng: Writing – original draft, Methodology, Formal analysis, Conceptualization. **Jin-Yu Qiao:** Investigation, Formal analysis. **Hong-Ming Zhang:** Methodology, Investigation. **Xiao-Fang Shen:** Writing – review & editing, Funding acquisition. **Yue-Hong Pang:** Writing – review & editing, Validation, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (22276077, 22076067).

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2024.138802.

References

Alampanos, V., Kabir, A., Furton, K. G., Panderi, I., & Samanidou, V. (2022). Capsule phase microextraction of six bisphenols from human breast milk using a monolithic polyethylene glycol sorbent-based platform prior to high performance liquid chromatography-photo-diode array detection determination. *Journal of Chromatography A, 1685*, Article 463615. https://doi.org/10.1016/j.chroma.2022.463615

Almeida, S., Raposo, A., Almeida-González, M., & Carrascosa, C. (2018). Bisphenol A: Food exposure and impact on human health. *Comprehensive Reviews in Food Science and Food Safety, 17*(6), 1503–1517. https://doi.org/10.1111/1541-4337.12388

Association of Official Analytical Chemistry (AOAC) (2012). Guidelines for single laboratory validation of chemical methods for dietary supplements and botanicals.

Catenza, C. J., Farooq, A., Shubear, N. S., & Donkor, K. K. (2021). A targeted review on fate, occurrence, risk and health implications of bisphenol analogues. *Chemosphere, 268*, Article 129273. https://doi.org/10.1016/j.chemosphere.2020.129273

Chang, Q., Zang, X., Wu, T., Wang, M., Pang, Y., Wang, C., & Wang, Z. (2019). Use of functionalized covalent organic framework as sorbent for the solid-phase extraction of biogenic amines from meat samples followed by high-performance liquid chromatography. *Food Analytical Methods, 12*(1), 1–11. https://doi.org/10.1007/s12161-018-1324-9

Chinese Pharmacopoeia Commission (ChP) (2020). Pharmacopoeia of the People's Republic of China.

Chen, D., Kannan, K., Tan, H., Zheng, Z., Feng, Y. L., Wu, Y., & Widelka, M. (2016). Bisphenol analogues other than BPA: Environmental occurrence, human exposure, and toxicity - A review. *Environmental Science and Technology, 50*, 5438–5453. https://doi.org/10.1021/acs.est.5b05387

Côté, A. P., Benin, A. I., Ockwig, N. W., O'Keeffe, M., Matzger, A. J., & Yaghi, O. M. (2005). Chemistry: Porous, crystalline, covalent organic frameworks. *Science, 310* (5751), 1166–1170. https://doi.org/10.1126/science.1120411

Das, S. K., Bhunia, K., Mallick, A., Pradhan, A., Pradhan, D., & Bhaumik, A. (2018). A new electrochemically responsive 2D Π-conjugated covalent organic framework as a high performance supercapacitor. *Microporous and Mesoporous Materials, 266*, 109–116. https://doi.org/10.1016/j.micromeso.2018.02.026

Deng, Z. H., Li, N., Jiang, H. L., Lin, J. M., & Zhao, R. S. (2019). Pretreatment techniques and analytical methods for phenolic endocrine disrupting chemicals in food and environmental samples. *TrAC - Trends in Analytical Chemistry, 119*, Article 115592. https://doi.org/10.1016/j.trac.2019.07.003

Dong, L. J., Tan, Z. Q., Chen, M., & Liu, J. F. (2015). Hollow fiber supported liquid membrane coupled with high performance liquid chromatography for highly sensitive determination of bisphenols in environmental water samples. *Analytical Methods, 7*(4), 1380–1386. https://doi.org/10.1039/c4ay02635g

Gallo, P., Di Marco Pisciottano, I., Esposito, F., Fasano, E., Scognamiglio, G., Mita, G. D., & Cirillo, T. (2017). Determination of BPA, BPB, BPF, BADGE and BFDGE in canned energy drinks by molecularly imprinted polymer cleaning up and UPLC with fluorescence detection. *Food Chemistry, 220*, 406–412. https://doi.org/10.1016/j.foodchem.2016.10.005

Grimaldi, M., Boulahtouf, A., Toporova, L., & Balaguer, P. (2019). Functional profiling of bisphenols for nuclear receptors. *Toxicology, 420*, 39–45. https://doi.org/10.1016/j.tox.2019.04.003

Han, S., Song, Y., Hu, J., Liu, R., Chi, Y., Kang, A., Deng, H., & Zhu, D. (2021). Novel computer-assisted separation prediction strategy for online enrichment-HPLC-FLD in simultaneous monitoring of bisphenols in children's water bottles. *Food Chemistry, 339*, Article 127766. https://doi.org/10.1016/j.foodchem.2020.127766

Hercog, K., Maisanaba, S., Filipič, M., Sollner-Dolenc, M., Kač, L., & Žegura, B. (2019). Genotoxic activity of bisphenol A and its analogues bisphenol S, bisphenol F and bisphenol AF and their mixtures in human hepatocellular carcinoma (HepG2) cells. *Science of the Total Environment, 687*, 267–276. https://doi.org/10.1016/j.scitotenv.2019.05.486

Jemmeli, D., Marcoccio, E., Moscone, D., Dridi, C., & Arduini, F. (2020). Highly sensitive paper-based electrochemical sensor for reagent free detection of bisphenol A. *Talanta, 216*, Article 120924. https://doi.org/10.1016/j.talanta.2020.120924

Kannouma, R. E., Hammad, M. A., Kamal, A. H., & Mansour, F. R. (2022). Miniaturization of Liquid-Liquid extraction; the barriers and the enablers. *Microchemical Journal, 182*, Article 107863. https://doi.org/10.1016/j.microc.2022.107863

Karak, S., Dey, K., & Banerjee, R. (2022). Maneuvering applications of covalent organic frameworks via framework-morphology modulation. *Advanced Materials, 34*, 202202751. https://doi.org/10.1002/adma.202202751

Li, J., Li, H., Zhang, W. J., Wang, Y. B., Su, Q., & Wu, L. (2018a). Hollow fiber-stir bar sorptive extraction and gas chromatography-mass spectrometry for determination of organochlorine pesticide residues in environmental and food matrices. *Food Analytical Methods, 11*(3), 883–891. https://doi.org/10.1007/s12161-017-1053-5

Li, W., Xue, Y., Fu, X., Ma, Z., & Feng, J. (2022). Covalent organic framework reinforced hollow fiber for solid-phase microextraction and determination of pesticides in foods. *Food Control, 133*, Article 108587. https://doi.org/10.1016/j.foodcont.2021.108587

Li, Y., Lu, P., Cheng, J., Zhu, X., Guo, W., Liu, L., Wang, Q., He, C., & Liu, S. (2018b). Novel microporous β-cyclodextrin polymer as sorbent for solid-phase extraction of bisphenols in water samples and orange juice. *Talanta, 187*, 207–215. https://doi.org/10.1016/j.talanta.2018.05.030

Liu, J., Zhang, L., Lu, G., Jiang, R., Yan, Z., & Li, Y. (2021). Occurrence, toxicity and ecological risk of Bisphenol A analogues in aquatic environment - A review. *Ecotoxicology and Environmental Safety, 208*, Article 111481. https://doi.org/10.1016/j.ecoenv.2020.111481

Liu, T., Wang, Q., Kong, J., Zhang, L., Qian, F., Gao, M., Ding, Y., Dahlgren, R. A., & Wang, X. (2022a). Enhanced adsorption/extraction of bisphenols by pyrrolic N-based 3D magnetic carbon nanocomposites for effervescence-assisted solid-phase microextraction of bisphenols from juices and the underlying interaction mechanisms. *Chemical Engineering Journal, 448*, Article 137690. https://doi.org/10.1016/j.cej.2022.137690

Liu, Z., Zhou, W., Hong, Y., Hu, W., Li, Z., & Chen, Z. (2022b). Covalent organic framework-V modified porous polypropylene hollow fiber with detachable dumbbell-shaped structure for stir bar sorptive extraction of benzophenones. *Journal of Chromatography A, 1664*, Article 462798. https://doi.org/10.1016/j.chroma.2021.462798

Ma, Y., Liu, H., Wu, J., Yuan, L., Wang, Y., Du, X., Wang, R., Marwa, P. W., Petlulu, P., Chen, X., & Zhang, H. (2019). The adverse health effects of bisphenol A and related toxicity mechanisms. *In Environmental Research, 176*, Article 108575. https://doi.org/10.1016/j.envres.2019.108575

Ocaña-Rios, I., de Jesús Olmos-Espejel, J., & Donkor, K. K. (2022). Recent advances in analysis of bisphenols and their derivatives in biological matrices. *Analytical and Bioanalytical Chemistry, 414*, 807–846. https://doi.org/10.1007/s00216-021-03668-y

Owczarek, K., Waraksa, E., Kłodzińska, E., Zrobok, Y., Ozimek, M., Rachoń, D., Kudłak, B., Wasik, A., & Mazerska, Z. (2022). Validated GC-MS method for determination of bisphenol a and its five analogues in dietary and nutritional supplements. *Microchemical Journal, 180*, Article 107643. https://doi.org/10.1016/j.microc.2022.107643

Pang, Y. H., Yue, Q., Huang, Y. Ying, Yang, C., & Shen, X. F. (2020). Facile magnetization of covalent organic framework for solid-phase extraction of 15 phthalate esters in beverage samples. *Talanta, 206*, Article 120194. https://doi.org/10.1016/j.talanta.2019.120194

Qu, J., Li, Y., Gao, M., Tan, C., Li, J., Wang, X., & Wang, H. (2019). Development and optimization of a thiol imidazolium-based ionic liquid for ultrasonic assisted liquid-liquid microextraction combined with HPLC-FLD for determination of bisphenols in milk and juice samples. *LWT, 111*, 653–662. https://doi.org/10.1016/j.lwt.2019.05.096

Segura, J. L., Royuela, S., & Mar Ramos, M. (2019). Post-synthetic modification of covalent organic frameworks. *Chemical Society Reviews, 48*, 3903–3945. https://doi.org/10.1039/c8cs00978c

Song, Y., Sun, Q., Aguila, B., & Ma, S. (2019). Opportunities of covalent organic frameworks for advanced applications. *Advanced Science, 6*, 1801410. https://doi.org/10.1002/advs.201801410

Vaghela, C., Kulkarni, M., Karve, M., & Zinjarde, S. (2022). Selective electrochemical sensing of bisphenol derivatives using novel bioelectrode of agarose-guar gum-graphene oxide immobilized with tyrosinase. *Journal of Environmental Chemical Engineering, 10*(3), Article 107360. https://doi.org/10.1016/j.jece.2022.107360

Xia, L., Du, Y., Xiao, X., & Li, G. (2019). One-step membrane protected micro-solid-phase extraction and derivatization coupling to high-performance liquid chromatography for selective determination of aliphatic aldehydes in cosmetics and food. *Talanta, 202*, 580–590. https://doi.org/10.1016/j.talanta.2019.05.035

Xiong, L., Yan, P., Chu, M., Gao, Y., Li, W., & Yang, X. (2018). A rapid and simple HPLC-FLD screening method with QuEChERS as the sample treatment for the simultaneous monitoring of nine bisphenols in milk. *Food Chemistry, 244*, 371–377. https://doi.org/10.1016/j.foodchem.2017.10.030

Xu, T., Zhang, R., Bi, Y., Li, J., Li, X., Chen, L., & Fang, Z. (2022). Electrospun polycrown ether composite nanofibers as an adsorbent for on-line solid phase extraction of eight bisphenols from drinking water samples with column-switching prior to high performance liquid chromatography. *Polymers, 14*(21), 4765. https://doi.org/10.3390/polym14214765

Yamini, Y., Faraji, M., & Ghambarian, M. (2015). Hollow-fiber liquid-phase microextraction followed by gas chromatography flame ionization detection for the determination of amitraz in honey and water samples. *Food Analytical Methods, 8*(3), 758–766. https://doi.org/10.1007/s12161-014-9953-0

Zhang, N., Ishag, A., Li, Y., Wang, H., Guo, H., Mei, P., Meng, Q., & Sun, Y. (2020). Recent investigations and progress in environmental remediation by using covalent organic framework-based adsorption method: A review. *Journal of Cleaner Production, 277*, Article 123360. https://doi.org/10.1016/j.jclepro.2020.123360

Zhang, X., Zhu, D., Huang, C., Sun, Y., & Lee, Y. (2015). Sensitive detection of bisphenol A in complex samples by in-column molecularly imprinted solid-phase extraction coupled with capillary electrophoresis. *Microchemical Journal, 121*, 1–5. https://doi.org/10.1016/j.microc.2015.01.012

Zhang, Y., Yuan, Z. L., Deng, X. Y., Wei, H. D., Wang, W. L., Xu, Z., Feng, Y., & Shi, X. (2022). Metal-organic framework mixed-matrix membrane-based extraction combined HPLC for determination of bisphenol A in milk and milk packaging. *Food Chemistry, 386*, Article 132753. https://doi.org/10.1016/j.foodchem.2022.132753