Urea-linked covalent organic framework functionalized polytetrafluoroethylene film for selective and rapid thin film microextraction of rhodamine B

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A B S T R A C T

Incorporation of highly selective and stable adsorbent with facile extraction technology is desired in practical analysis. Here we show the rational preparation of a urea-linked covalent organic framework functionalized polytetrafluoroethylene film (COF-117-PTFE) with ordered porous structure, rich functional groups, and large surface area-to-volume ratio as the effective adsorbent for convenient, selective and rapid thin film microextraction (TFME) of rhodamine B (RB). The COF-117-PTFE based TFME coupled with high performance liquid chromatography-fluorescence detector (HPLC-FLD) successfully realized the determination of RB with the limit of detection of 0.007 μg L^{-1}, the linear range of 0.1 - 100 μg L^{-1}. The relative standard deviation (RSD) of intraday ($n = 5$) and interday ($n = 5$) for the determination of 10 μg L^{-1} RB were 2.3% and 6.8%, respectively. The absolute recoveries were 80.3%, 71.2% and 67.9% in river water, chili powder and Sichuan pepper powder, respectively. The recoveries for RB spiking in complicated real samples (dry chili, chili powder, dry Sichuan pepper, Sichuan pepper powder and river water) ranged from 90.4% to 107.5%. The developed COF-117-PTFE based TFME-HPLC-FLD method is promising in practical application. This work reveals the high potential of functionalized COF film as the adsorbent for effective extraction of trace contaminants in complicated samples.

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1. Introduction

Rhodamine B (RB) is a well-known synthetic xanthene dye and widely used in textile, printing, and plastic due to its low price, high color fastness, and great stability [1,2]. As a result, RB is easily accumulated in the aquatic environment [3]. Trace RB exhibits high reproductive and developmental toxicity as well as neurotoxicity to human and animals [4–7]. International Agency for Research on Cancer identified RB as carcinogen III in 1987 [8]. RB was also proved to be genotoxic and carcinogenic by European Food Safety Authority [9]. However, compared with the other synthetic dyes such as Congo red and methyl blue, RB always serves as illegal addition in foodstuffs such as chili and pepper to promote the sensory properties owing to its special bright red color and color fastness [2,10,11]. Consequently, development of rapid and

sensitive methods for precise determination of trace RB is great of significance for the environment and food. Although fluorescence spectrophotometry, electrochemical sensing and ultraviolet-visible spectrophotometry have been applied to determination of RB [12–14], high-performance liquid chromatography (HPLC) is still proved to be the most common technique for the determination of RB owing to its high accuracy and reproducibility [15–17].

The trace level of RB along with serious interferences from complicated matrixes makes sample pretreatment necessary before HPLC analysis. However, sample pretreatment procedures are usually time-consuming and error-prone [18]. Solid phase extraction (SPE) is a widely used technique for sample pretreatment. As the core of SPE, adsorbent dominates the extraction performance. Lots of novel materials including ionic liquid-cyclodextrin cross-linked polymer [19], functionalized magnetic graphene oxide [20], functionalized carbon nanotubes [21], and molecularly imprinted polymers [22,23] have been devoted as adsorbents of SPE, magnetic SPE and solid-phase microextraction to promote the extraction performance of RB. The incorporation of highly selective and stable adsorbent with facile extraction technologies is still desired

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for determination of RB in complicated samples. Thin film solid phase microextraction (TFME) was developed by Pawliszyn et al. in 2003 [24]. The film with large surface area-to-volume ratio in TFEM makes the solid coating thinner than that of on the fiber of solid phase microextraction, promoting the extraction rate. TFME is considered to be an attractive extraction technique due to its simple operation, high extraction efficiency and low organic solvent consumption [25,26].

Covalent organic frameworks (COFs) are an emerging class of porous crystalline polymers consisting of pure organic units with covalent bonds [27]. The ordered pore structure, large surface area and good chemical stability make COFs promising as adsorbents in sample pretreatment with good selectivity, large adsorption capacity and rapid kinetics [28–31]. Thus, the application of COFs in TFME should be practical and promising for sample pretreatment, but has not been explored so far.

Herein, we report the fabrication of urea-linked COF functionalized polytetrafluoroethylene (PTFE) film (urea-linked COF-PTFE) as the adsorbent of TFME for selective and rapid extraction of RB. Urea-linked COF (COF-117) was selected because it has rich urea and aromatic groups as multiple active sites for hydrogen bonding, electrostatic and π-π interaction to promote the selectivity for the extraction of RB [32–34]. COF-117 was covalently grafted onto PTFE film to obtain COF-117-PTFE for the TFME of RB. Thus, a COF-117-PTFE based TFME method was developed and coupled with high-performance liquid chromatography-fluorescence detector (HPLC-FLD) for the determination of trace RB in real samples. This work conveys the high potential of COFs functionalized membrane as the adsorbent for effective extraction of trace contaminants in complicated samples.

2. Experimental section

2.1. Synthesis of COF-117-PTFE

Typically, 20 pieces of spherical PTFE film (diameter of 13 mm) was ultrasonically treated with ethanol (EtOH) for 20 min. The treated PTFE film was immersed in dopamine solution containing 40 mg DA and 10 mL 9 mM Tris–HCl buffer (pH 8.5), and vibrated at 60 °C for 5 h, then soaked in ultrapure water for 24 h and dried to obtain the polydopamine coated PTFE film (pDA-PTFE). The pDA-PTFE was further reacted with 50 mg Tp in 50 mL 1,4-dioxane at 90 °C for 1 h, then rinsed with DMF and EtOH to get Tp-PTFE. Based on the conditions for the synthesis of COF-117 [32], 10 pieces of Tp-PTFE were sonicated with pre-polymerization solution containing Tp (40 mg), BDU (55.5 mg), NMP (1.6 mL), TCB (0.4 mL), acetic acid (6 M, 0.2 mL) in a 35-mL Schlenk tube (OD 26 × L 125 mm) for 15 min, reacted at 85 °C for 1 day, washed sequentially with DMF, EtOH, and ultrapure water, then freeze-dried under vacuum for 2 h to get COF-117 grafted PTFE film (COF-117-PTFE).

2.2. Sample preparation

Real samples of chili, chili powder, Sichuan pepper and Sichuan pepper powder were collected from local supermarkets. Typically, 1 g of the dried solid sample was mixed with 5.0 mL of methanol (MeOH)/0.1% formic acid (FA) aqueous solution (1/1, v/v) in a 10 mL centrifuge tube, and vortexed for 15 min for twice. The supernatant was collected via centrifugation at 8000 rpm for 5 min, and dried with N_2 flow. The obtained residue was dissolved with 3.0 mL of 3% NaCl solution (w/v, pH 3.0) for further extraction. The river water was filtered through 0.45 μm membrane, then dried with N_2 flow, also redissolved with 3.0 mL of 3% NaCl solution (w/v, pH 3.0) prior to extraction.

2.3. TFME procedure

Typically, one piece of COF-117-PTFE was placed in 3 mL sample solution or standard solution, vortexed for 20 min. Then, the COF-117-PTFE was transferred into a 2 mL centrifuge tube, 1 mL of MeOH/FA (9/1, v/v) was mixed with the film under vortex for 2 min to elute the adsorbed RB from the COF-117-PTFE. The eluent was separated by centrifugation, dried under a N_2 stream, redissolved with 200 μL of MeOH /FA (9/1, v/v), and filtered on 0.22 μm membrane for HPLC analysis.

2.4. HPLC analysis

HPLC analysis was performed on an e2695 HPLC equipped with a 2475 fluorescence detector (Waters, USA). 10 μL of extracted sample solution was injected, separated on an X Bridge C18 column (250 mm × 4.6 mm I.D., 5 μm) (Waters, USA) with 1.0 mL min^{-1} of MeOH/0.1% FA aqueous solution (70/30, v/v) as the mobile phase at 35 °C for 10 min, and detected at an emission wavelength of 574 nm under excitation at 553 nm.

3. Results and discussion

3.1. Preparation of COF-117-PTFE

To promote the extraction efficiency, we proposed an in-situ growth strategy for the preparation of COF-117-PTFE for TFME of RB (Fig 1). PTFE film was first modified with DA to obtain pDA-PTFE with the amino groups. Then, Tp was grafted on the PTFE via a condensation of the amino groups in pDA-PTFE and the aldehyde groups in Tp to get Tp-PTFE. Finally, the pre-polymerization solution containing Tp and BDU was further reacted with Tp-PTFE to obtain COF-117-PTFE. The proposed in-situ growth strategy ensures the formation of stable continuous COF-117 film on the PTFE film for extraction [35].

3.2. Characterization of COF-117-PTFE

The prepared COF-117-PTFE was first characterized by FTIR spectroscopy (Fig 2a). pDA-PTFE gave obvious peaks at 1519 and 1602 cm^{-1} for the N–H vibration of the primary amide, indicating the successful modification of amino groups on PTFE. The disappearance of the peaks of primary amide in the FTIR spectra of Tp-PTFE confirms the successful graft of Tp. Finally, the obvious peak for the C = O of urea (1729 cm^{-1}) and the other peaks of COF-117 in FTIR spectra of COF-117-PTFE prove the successful in-situ growth of COF-117 on PTFE [32].

SEM images directly show the morphology change of the PTFE film during modification. pDA-PTFE, Tp-PTFE and COF-117-PTFE showed evidently distinguishable morphology with the original PTFE film (Fig 2b, and S1-S3). Importantly, a dense COF-117 layer with network-like structure appeared on the surface of PTFE, further conveying the uniform growth of COF-117 on the PTFE film (Fig 2b and S4).

The static contact angle was applied to evaluate the hydrophilicity of the films. As shown in Fig 2c and S5, the contact angle of 100.5° ± 1.3° reveals the weak hydrophobicity of PTFE due to the composition of $[-(-CF_2-CF_2-)_n-]$ [36]. The introduction of hydrophilic groups such as amino group and hydroxyl group led to the decrease of the contact angle for pDA-PTFE (63.3° ± 3.8°). Tp-PTFE became more hydrophobic (81.0° ± 2.5°) because of the introduced additional benzene rings [37]. The strong hydrophilicity of COF-117 with rich hydrophilic urea groups (17.2° ± 2.2°) changed the film from hydrophobicity (100.5° ± 1.3° for PTFE) to hydrophilicity (30.0° ± 2.4° for COF-117-PTFE).
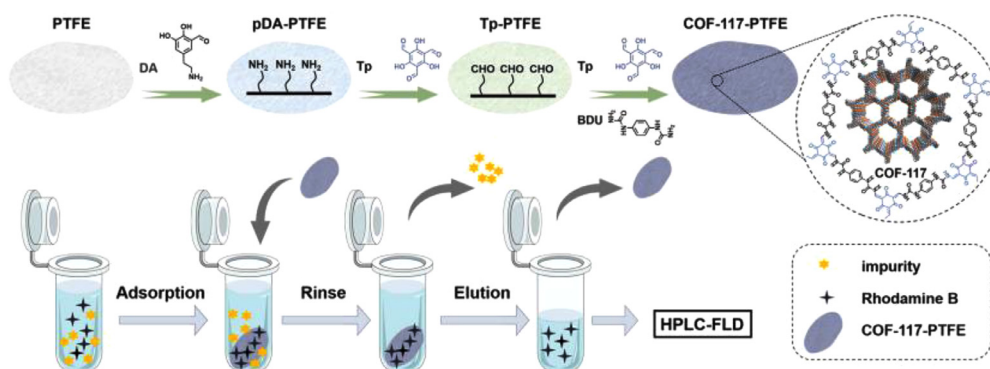
Fig 1. Schematic representation for the synthesis of COF-117-PTFE and its based TFME process.
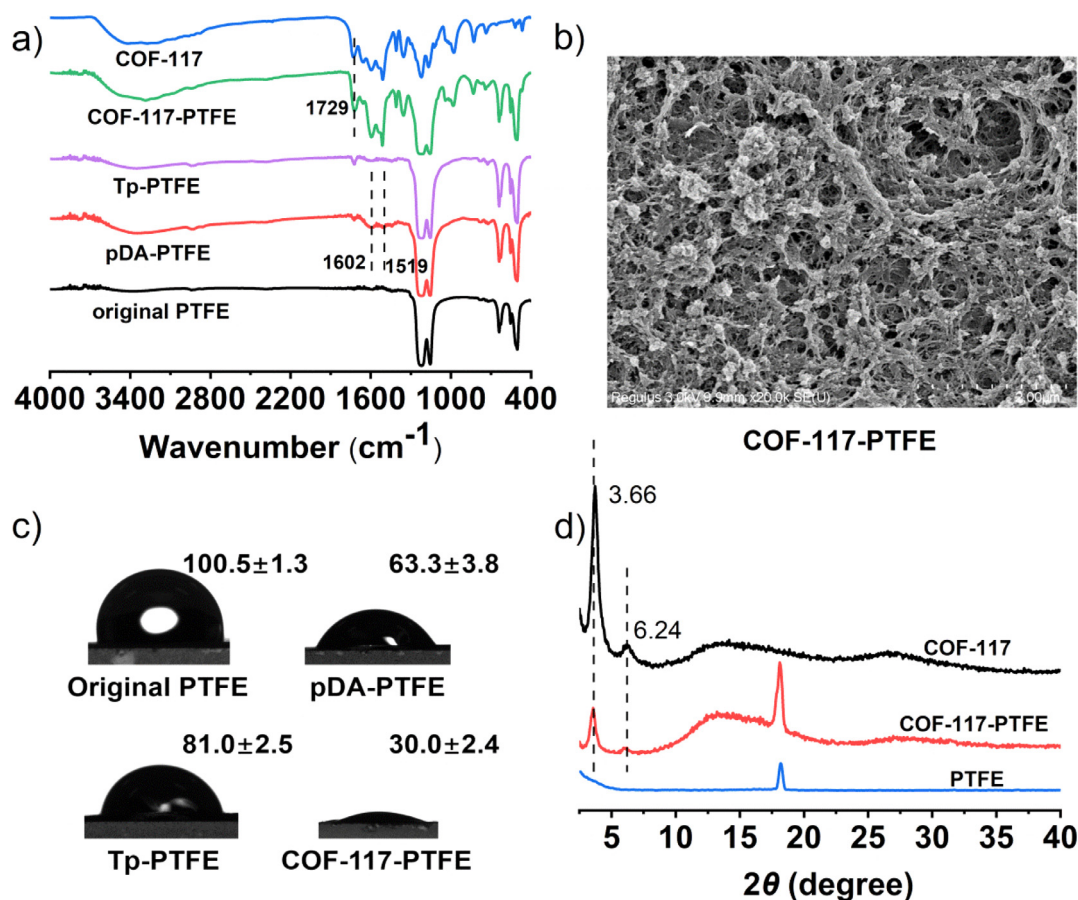

Fig 2. (a) FT-IR spectra, (b) SEM image, (c) contact angles and (d) PXRD patterns of films.

The ordered porous structure is essential to the promotion of adsorption efficiency. Thus, it is important to confirm the crystallinity of the bonded COF-117 on the PTFE. Except the characteristic peak of PTFE, COF-117-PTFE gave two obvious characteristic PXRD peaks (at 3.66° and 6.24°) for COF-117 [32], indicating the crystallinity of COF-117 on the PTFE (**Fig 2d**). The characteristic PXRD pattern of COF-117 still remained even in various solvents including MeOH, EtOH, acetonitrile, 0.1 M HCl and 0.1 M NaOH for 1 day, demonstrating the sufficient stability of the prepared COF-117 for further practical application (**Fig S6**). The Brunauer-Emmett-Teller surface area, the pore size and the capacity of COF-117 obtained from the N_2 adsorption experiment (**Fig S7**) were 68.5 m^2 g^{-1}, ca. 23.8 Å and 0.146 cm^3 g^{-1}, respectively.

3.3. Optimization of TFME procedure

The factors affecting the extraction efficiency of RB including temperature, extraction time, pH, ionic strength, eluent, eluent volume, and elution time were tested. The increase of temperature went against the extraction efficiency of RB, indicating that room temperature was suitable for the extraction (**Fig S8**). Study on the effect of extraction time on the extraction efficiency of RB indicates that 20 min is sufficient for the adsorption of RB (**Fig 3a**). The two forms (cationic and zwitterionic forms) of RB under different pH values demonstrate the pH would affect the extraction [38]. As shown in **Fig 3b**, the extraction efficiency of RB decreased with the increase of pH from 3 to 5. Further increase the pH gave
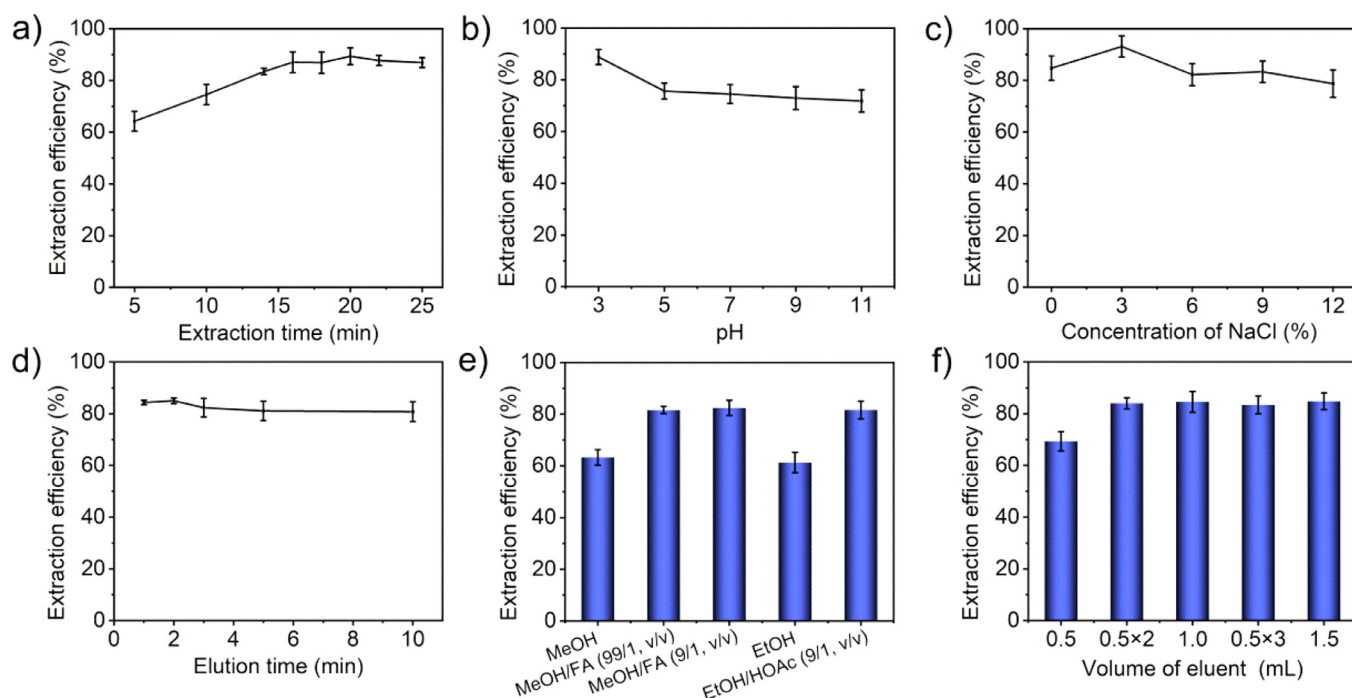
Fig 3. Effect of (a) extraction time, (b) pH, (c) ionic concentration, (d) elution time, (e) type of eluent, and (f) eluent volume on the extraction efficiency of RB (10 μg L^{-1}) with the COF-117-PTFE. All experiments were performed in triplicate.

no obvious negative effect on the extraction efficiency. Thus, pH 3 was chosen for the TFME.

The effect of ionic strength on the extraction was also examined. The extraction efficiency of RB increased with the concentration of NaCl from 0 to 3% (w/v), and then decreased with the further increase of the concentration of NaCl (**Fig 3c**), indicating the favor of 3% (w/v) of NaCl for extraction. Such result comes from the combined effects of salt out and ionic competition [39].

The investigation of elution time indicates the RB was completely desorbed from COF-117-PTFE in 2 min (**Fig 3d**). The mixture of acid and organic solvent gave larger extraction efficiency than the single organic solvent [22]. MeOH/FA (9:1, v/v) was finally chosen as the eluent due to the highest extraction efficiency (**Fig 3e**). The eluent volume of 0.5 mL $\times$ 2, 1 mL, 0.5 mL $\times$ 3, 1.5 mL was sufficient to elute the RB from the COF-117-PTFE (**Fig 3f**). Thus, the elution was performed with 1 mL of MeOH/FA (9:1, v/v) for 2 min.

3.4. Analytical figures of merit

The analytical performance of COF-117-PTFE for the TFME of RB under the optimal conditions was evaluated. The calibration curve (the peak area of RB against the concentration of RB in standard solution) was linear in the range of 0.1 - 100 μg L^{-1} (R^2 = 0.9994) (**Fig S9**). The limit of detection (LOD) ($S/N = 3$) and limit of quantification (LOQ) ($S/N = 10$) of the developed COF-117-PTFE based TFME-HPLC-FLD for RB were found to be 0.007 and 0.02 μg L^{-1}, respectively. The relative standard deviation (RSD) of intraday ($n = 5$) and interday ($n = 5$) for the determination of 10 μg L^{-1} RB were 2.3% and 6.8%, respectively. The extraction efficiency of RB remained above 87.7% after four cycle continuous extractions, indicating the great reusability of the prepared COF-117-PTFE (**Fig 4a**).

The anti-interference ability is a key factor of adsorbent for the precise analysis. In practice, the substances including Vitamin C, citric acid, capsanthin, Sudan I, Sudan III, amaranth, methyl orange and methyl blue are potential interferents for the determination of RB in the real samples (chili and Sichuan pepper) [13,40]. Study on

the effect of these substances on the determination of RB showed that even 1000 times higher concentration of the interferents than RB gave negligible effect on the detection of RB (**Fig 4b**), demonstrating the high selectivity of COF-117-PTFE.

Compared with other reported adsorbents based SPE such as polypyrrole functionalized nanofibers mat [41], magnesium hydroxide/carbon nanotube composites [42], and silicon dioxide nanocomposite coated with graphene-like boron nitride nanosheet [1], our proposed COF-117-PTFE based TFME-HPLC-FLD method exhibited lower or comparable LOD (**Table S1**). In addition, the more convenience of the TFME with less organic solvent consumption make our method high potential for the determination of RB in real samples.

3.5. Mechanism

To figure out the mechanism of the great extraction of RB on COF-117-PTFE, the zeta potential of COF-117 was measured (**Fig S10**). The dispersed COF-117 was negatively charged in the pH range of 3–10. As we mentioned, RB is a compound with ionizable polar groups. When solution pH is higher than 3.2 (pKa of RB) [1], the cation form of RB starts to convert to amphoteric ionic form (**Fig S11**) [38,43]. Meanwhile, the extraction efficiency of RB started to decrease with the increase of pH from 3 to 5 and then kept stable, indicating the dominant electrostatic interaction in the extraction of RB. Moreover, the rich aromatic group and urea in COF-117 can provide abundant hydrogen bonding sites and π-π interaction to promote the selectivity of the COF-117-PTFE to RB [33,34].

3.6. Real sample analysis

The developed COF-117-PTFE based TFME-HPLC-FLD was further applied to the determination of RB in the samples of chili, chili powder, Sichuan pepper, Sichuan pepper powder and river water. The matrix effect (ME) of the river water was 97.8% and 95.9% at 10 and 50 μg L^{-1} RB, indicating the availability of standard calibration curve for the analysis of the river water. However, the chili
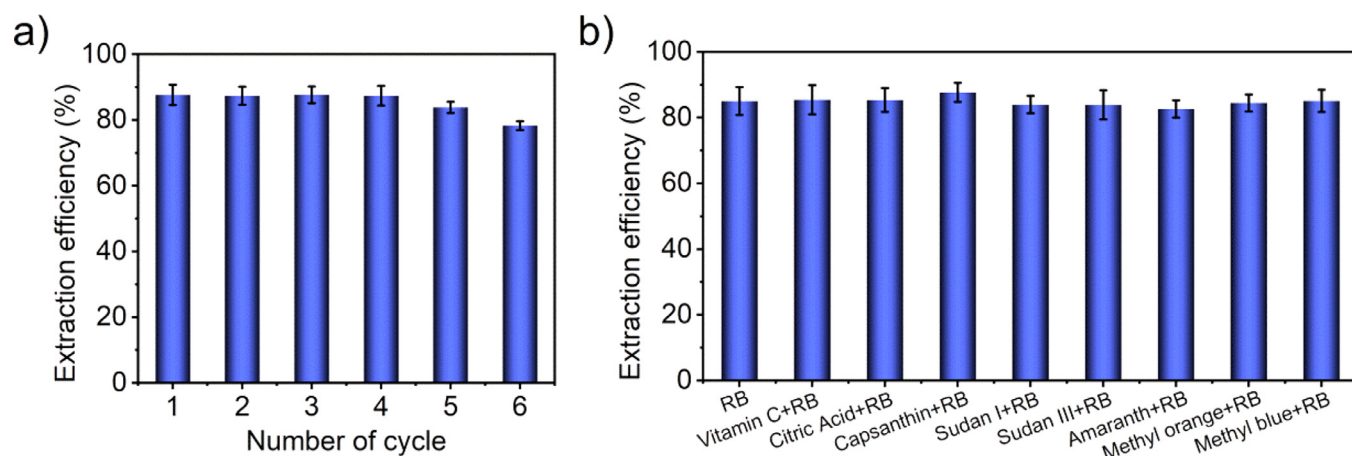
Fig 4. Effect of (a) number of cycle and (b) potential interferents on the extraction efficiency of RB (10 $\mu g\ L^{-1}$) with the COF-117-PTFE. All experiments were performed in triplicate.

Table 1
Analytical results for the determination of RB in real samples.

Sample	Spiked RB ($\mu g\ kg^{-1}$)	Determined RB ($\mu g\ kg^{-1}$) mean ± $s, n = 5$	Spiking Recovery (%, mean ± $s, n = 5$)
Dried Chili	0	ND[a]	–
	5	4.84 ± 0.32	96.8 ± 6.4
	50	45.2 ± 4.1	90.4 ± 8.2
	200	204 ± 7	102 ± 4
Chili powder I	0	<LOQ	–
	5	4.65 ± 0.32	93.0 ± 6.4
	50	47.8 ± 1.4	95.6 ± 2.8
	200	184 ± 10	92.0 ± 5.0
Chili powder II	0	5.23 ± 0. 12	–
	5	9.84 ± 0.32	92.2 ± 6.4
	50	55.8 ± 4.9	101 ± 10
	200	192 ± 9	93.4 ± 4.5
Sichuan Pepper	0	ND[a]	–
	5	4.80 ± 0.37	96.0 ± 7.4
	50	47.8 ± 2.2	95.6 ± 4.4
	200	191 ± 13	95.5 ± 6.5
Sichuan Pepper powder	0	ND[a]	–
	5	4.80 ± 0.21	96.0 ± 4.2
	50	47.8 ± 2.7	95.6 ± 5.4
	200	183 ± 11	91.5 ± 5.5
River water	0	ND[a]	–
	5	4.92 ± 0.27	98.4 ± 5.4
	50	48.6 ± 3.5	97.2 ± 7.0
	200	215 ± 13	108 ± 7

[a] Not determined.

and Sichuan pepper at 10 and 50 $\mu g\ L^{-1}$ RB gave the ME of 50.7%, 48.6% and 46.2%, 47.3%, respectively, indicating the standard additions method was needed for the analysis of the chili and Sichuan pepper sample. The absolute recovery (AR) was 80.3%, 71.2% and 67.9% in river water, chili powder and Sichuan pepper powder, respectively. RB was found to be 5.23 ± 0.12 $\mu g\ kg^{-1}$ in chili powder II, whereas the concentration of RB in other samples were below the LOD or LOQ (**Table 1**). The spiking recoveries of RB in the six samples spiked with 5, 50, and 200 $\mu g\ kg^{-1}$ were in the range of 90.4%−107.5%. Furthermore, the proposed COF-117-PTFE based TFME-HPLC-FLD was applied to analyze a standard reference sample of chili powder (MRM0111) with the certified RB concentration of 16.5 ± 3.3 μg kg^{-1}. The good agreement of determined concentration of RB (15.2 ± 6.8 μg kg^{-1}, $n = 5$) with the certified value indicates the accuracy of the proposed method for the determination of RB.

4. Conclusion

In summary, we have prepared a urea-linked COF functionalized PTFE via the in-situ growth method. The conjunction of ordered structure, rich urea functionality and great stability of COF-117 with large surface area-to-volume ratio of PTFE offers the high potential of the prepared COF-117-PTFE as the adsorbent for TFME of RB. The developed COF-117-PTFE based TFME coupled with HPLC-FLD provides a promising method for the determination of RB in various samples. This work conveys the high potential application of COFs functionalized film as adsorbent for effective TFME of trace pollutants in complicated environmental and food samples.

Appendix A. Supplementary data
Supplementary data to this article can be found online at XXX.

Declaration of Competing Interest

The authors declare no competing financial interest.

Acknowledgments

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2022.463133.

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