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Ronglin Wang , Canru Li , Qianlian Li , Sunxian Zhang , Feng lv ,
Zhiming Yan

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Highlights

- PT-SPE was used for the extraction of tetracycline antibiotics for the first time.
- A novel COFs composite electrospun nanofibers was developed.
- The proposed PT-SPE/HPLC method was simple, facile and sensitive.

Electrospinning fabrication of covalent organic framework composite nanofibers for pipette tip solid phase extraction of tetracycline antibiotics in grass carp and duck

Ronglin Wang[1], Canru Li[1], Qianlian Li[1], Sunxian Zhang[2], Feng lv[1]*, Zhiming Yan[1]*

[1] Collge of Food Science, Fujian Agriculture and Forestry University, 350002, Fuzhou, Fujian, China

[2] Fujian inspection and research institute for product quality, 350001, Fuzhou, Fujian, China

Corresponding author: Zhiming Yan, Feng lv

Tel/Fax: 86-591-22688165

E-mail: 45765545@qq.com (ZH.M.Yan); 1245075427@qq.com (F. Lv)

Abstract: In the current study, a novel covalent organic frameworks COF-SCU1 incorporated electrospun nanofibers (PAN@COF-SCU1 nanofibers) was fabricated via a facile electrospinning method and utilized as adsorbent in pipette tip solid-phase extraction (PT-SPE) of tetracycline antibiotics (TCs) from foods. The prepared PAN@COF-SCU1 nanofibers possessed both of the unique characteristics of electrospun nanofibers and COFS-CU1, and thus improving the adsorption capacity of the electrospun nanofibers and preventing the problems of leakage and high pressure caused by directly using the nanosize COFs as adsorbent in PT-SPE. The experiments affected the adsorption and desorption efficiencies, such as the loading ratios of COFS-CU1 in nanofibers, the amount of nanofibers, the matrix pH and desorption solvent, were studied in detail. Eventually, a new pipette tip solid-phase extraction-high performance liquid chromatography (PT-SPE/HPLC) method was proposed for the analysis of three TCs from food. Satisfied linearity for TCs was obtained in the range of 4-70 ng mL^{-1}. The limits of detection and quantification were ranged from 0.6 to 3 ng mL^{-1} and from 2 to 10 ng mL^{-1}, respectively. The interday and intraday precisions (RSD) were all lower than 9%. The proposed PT-SPE/HPLC method was used to determine TCs residues in grass carp and duck samples for the first time. The results could not only explore the availability of PT-SPE in the extraction of TCs in food samples, but also broadened the potential applications of COFs in sample preparation.

Key words: Tetracycline antibiotics; Pipette tip solid phase extraction; Electrospun nanofibers; Covalent organic frameworks; High performance liquid chromatography.

1. Introduction

Tetracycline antibiotics (TCs), such as oxytetracycline (OTC), tetracycline (TC) and chlortetracycline (CTC), are a class of broad spectrum antibiotics and have been extensively applied in the aquaculture industry to prevent and treat various bacterial infectious diseases because of its wide spectrum, good water solubility and low price[1, 2]. However, the excessive and improper use of TCs in the aquaculture industry could cause TCs residues in foods, which lead to serious threats to human health, such as anaphylactic reaction, double infection, teratogenicity, liver damage and gastrointestinal disturbance[3]. Therefore, more and more countries have established stringent regulations on the maximum residue limits (MRL) for TCs residue in food to ensure food safety and protect consumers from TCs residues[4, 5]. Consequently, monitoring antibiotic residues in food especially with animal origin has attracted great attention in the past decades.

Routine monitoring of the TCs residues in food matrices could be carried out using a number of analytical methods, and high performance liquid chromatography (HPLC) combined with various detectors are usually used as confirmatory methods for the analysis of TCs[5, 6]. Additionally, an efficient sample preparation is a crucial step prior to HPLC analysis of TCs because of the low concentration of TCs and matrix effect in foods. To date, various sample preparation methods, such as solid-phase extraction (SPE)[7], liquid-liquid extraction (LLE)[8], magnetic solid-phase extraction (MSPE)[9] and in-tube solid-phase microextraction (SPME)[10], have been applied in the extraction of TCs in foods. Among these methods, SPE has been considered as one of the most powerful and most widely used method due to its merits of high recovery, simple operation, and easiness automation. In the past decade, the trends in SPE method focused on miniaturizing processes that use small amounts of adsorbent, minimal sample and solvent consumption[11]. Pipette tip solid-phase extraction (PT-SPE) is a novel form of SPE by using pipette tip as SPE cartridge, which requires tiny amount of adsorbent and thus significantly reduces the sample and solvent consumption[12, 13]. To the best of our knowledge, the application of PT-SPE for the extraction of TCs in foods has never been reported. On the other hand, the adsorbent is a key factor in the PT-SPE procedure which determine the extraction efficiency of analytes[14]. Therefore, it is of vital importance to develop novel adsorbent with good adsorption performance and utilize it as PT-SPE adsorbent for effective extraction of TCs in food matrices.

Covalent organic frameworks (COFs) are a novel class of crystalline porous material, which are composed of light elements such as C/H/O/N/B[15]. COFs possess large specific surface area, low density, controllable pore structure and good thermal and chemical stability, making them ideal candidates for a wide range of applications in gas adsorption, drug delivery, catalysis, sensing and separation[16, 17]. Recently, COFs have also been used as adsorbents in sample preparation. To date, most of the studies on the application of COFs in sample preparation focused on fabricating and utilizing pristine COFs as SPME coatings and magnetic COFs as MSPE adsorbents, respectively[18-25]. By comparison, the applications of COFs in other sample preparation methods including PT-SPE have been rarely reported. It is known that adsorbents with small particle size are difficult to be directly used as adsorbent in SPE-based methods due to the high back pressure[26]. Currently, there are few COFs with suitable particle size that could be used as adsorbents in SPE-based methods. Furthermore, COFs with small particle size tend to be agglomerated after drying due to high surface energy, which lead to the reduction of the available adsorption sites and weaken adsorption performance.

Electrospun nanofibers which was obtained from electrospinning technique, possessing some amazing features, such as large surface area to volume ratio, small size effect, and flexibility in surface functionalities[14, 27]. These unique merits of electrospun nanofibers make them good candidates as adsorbents in sample preparation with tiny amounts of adsorbent, sample and solvents[28]. Also, electrospun nanofibers have been used as substrate materials to fabricate composite nanofibers with improved adsorption performance in sample preparation[11, 29-32]. On the one hand, the utilization of composite electrospun nanofibers as adsorbents in SPE-based method could avoid the problems of high back pressure and leakages caused by the directly use of nanosized adsorbents. On the other hand, the incorporation of adsorbents with good adsorption performance could significantly increase the active adsorption sites of the electrospun nanofibers. Recently, we have firstly fabricated COFs incorporated electrospun nanofibers (PAN@SNW-1) and used it as PT-SPE adsorbent in the effective extraction of sulfonamides residues in meat samples. The results showed that small amounts of PAN@SNW-1 nanofibers and reduced solvents consumption could accomplish the whole sample preparation procedure. Encouraged by it, it is highly desirable to develop novel COFs based electrospun nanofibers and further explore its potential application in sample preparation.

Thus, the aim of the current study is to develop a novel polyacrylonitrile@COFs (PAN@COF-SCU1) electrospun composite nanofibers and investigate its potential application as the adsorbent in PT-SPE for effective extraction of TCs. COF-SCU1 (SCU stands for Sichuan University) was synthesized by forming CO-NH bonds between p-phenylenediamine and trimesoyl chloride[25]. Recently, COF-SCU1 has been utilized as SPME coating for the extraction of volatile benzene homologues from indoor air samples[25]. In this study, COF-SCU1 was fabricated using a facile and one-step synthetic method, and was further used to fabricate PAN@COF-SCU1 nanofibers via a simple co-electrospinning method. In addition, a series of factors that affected the adsorption and desorption efficiencies of PT-SPE based on PAN@COF-SCU1 nanofibers were studied systematically. Finally, the proposed PT-SPE coupled with HPLC method was successfully used for the determination of TCs in duck and grass carp samples.

2. Experimental

2.1 Reagents and chemicals

Triformyl chloride, polyacrylonitrile (PAN, Mw=150,000) and p-phenylenediamine were purchased from Aladdin Chemistry (Shanghai, China). Ethyl acetate (EA), anhydrous ethanol and ammonia were obtained from Xilong Scientific Co. Ltd. (Guangdong, China). Oxytetracycline, tetracycline and chlortetracycline were obtained from Macklin Biochemical (Shanghai, China). N,N-dimethylformamide (DMF), methanol and acetonitrile were purchased from Sinopharm Reagent (Shanghai, China). Duck and grass carp samples were obtained from local supermarket in Fuzhou.

2.2 Material characterization and HPLC conditions

Scanning electron microscopy (SEM) images were examined using an FEI QUANTA 430 field-emission scanning electron microscopy (FEI, USA). Transmission electron microscopy (TEM) images were measured by a FEI Tecnai

G20 transmission electron microscope (FEI, USA). Fourier transform infrared (FT-IR) spectras were recoreded using a Nicolet 6700 FT-IR spectrophotometer (Nicolet, USA). The specific surface area and pore diameter were analyzed by nitrogen adsorption on a Micromeritics ASAP 2020 porosimeter (Micromeritics, USA). Thermogravimetric analysis (TGA) was performed on a TGA Q500 thermogravimetric analyzer (TA Instruments, U.S.A.) under a nitrogen atmosphere from room temperature to 800 °C at a ramp rate of 10 °C min^{-1}. Zeta potentials were analysed on NanoBrook Omni Zeta potential analyzer (Brookhaven, NY, USA). The X-ray powder diffraction (XRD) patterns were characterized by a Bruker D8 Advance (Bruker, Germany) with Cu Kα source radiation over the angular range from 5 to 80°.

HPLC measurements were carried out using a Waters e2695 HPLC system equipped with 2998 PDA detector (Waters, USA) with the detection wavelength of 355 nm. Data acquisitions were performed by Empower Chromatography Software (Waters, USA). The analytical column (150 mm × 4.6 mm, VP-ODS, 5 μm) was supplied from Shimadzu (Kyoto, Japan). The mobile phase is methanol-acetonitrile-0.02mol L^{-1} oxalic acid (10:20:70, V/V) with a flow rate of 1.0 mL min^{-1}.

2.3 Preparation of COF-SCU1

COF-SCU1 was prepared according to the previous study with some modifications (Fig. 1a)[25]. Typically, 2.12 g trimethyl chloride was dissolved in 60 mL EA and 0.64 g p-phenylenediamine was dissolved in 30 mL EA, respectively. Then the p-phenylenediamine solution was added dropwise to the trimethyl chloride solution in 1 h at 0 ℃ with an ice-water bath. After reacting at room temperature for 24 h, the mixture solution was poured into 1 L ultrapure water and sonicated for 30 min. Then, the yellow product was collected by centrifugation, washed several times with ultrapure water and ethanol, respectively. Finally, the obtained products were redispersed in DMF for further experiments. For characterization, the COF-SCU1 dispersed in ethanol was dried under vacuum overnight at room temperature.

2.4 Preparation of PAN@COF-SCU1 nanofibers

The PAN@COF-SCU1 nanofibers with different loading of COF-SCU1 (10, 20 and 30%, respectively) were prepared via a co-electrospinning method. 6 mL DMF solution containing certain amounts of COF-SCU1 (71, 160, and 274mg, respectively) was sonicated for 0.5 h. Then, an amount of 0.64 g PAN powder was slowly added into the solution, and the mixture was stirred overnight to form a homogeneously dispersed PAN@COF-SCU1 spining solution with COF-SCU1 loading of 10, 20 and 30%, respectively. Subsequently, the prepared PAN@COF-SCU1 spining solution were poured into syringe with a 23 gauge needle tip. The tip-to-collector distance, the voltage and the flow rate were set at 15 cm, 18 kV and 1.0 mL h^{-1}, respectively. All the electrospinning process was performed at room temperature and relative humidity of 30%. The resultant nanofibers with different loading ratios of COF-SCU1 (10%, 20% and 30%) were referred to as PAN@COF-SCU1 (0.1), PAN@COF-SCU1 (0.2) and PAN@COF-SCU1 (0.3), respectively. Pure PAN nanofibers were also prepared via the same procedure with that of PAN@COF-SCU1 nanofibers but without adding COF-SCU1. All the prepared electrospun nanofibers were dried overnight at 80 ℃ to remove the possibly remaining solvents after electrospining.

2.5 Real samples preparation

Firstly, 10.0 g of samples (homogenized duck or grass carp) and 4 mL of ultrapure water were put into a 50 mL polypropylene centrifuge tube and were vortexed for 2 min. Then, 36 mL of formic acid/acetonitrile/water (0.1:90:9.9, V:V:V) mixture solution was added into the vortexed sample, and the mixture were sonicated for 30 min and centrifuged at 925 g for 5 min, respectively. Finally, the supernatant was evaporated by vacuum distillation, and the resultant solution was reconstituted to 40 mL with ultrapure water and stored in a refrigerator at 4 °C before use.

2.6 PT-SPE procedure

The schematic diagram of PT-SPE for the extraction of TCs based on PAN@COF-SCU1 nanofibers was demonstrated in Fig. 1b. Typically, 10 mg PAN@COF-SCU1 nanofibers was placed in a 0.2 mL pipette-tip, and absorbent cotton was set as frits at each side to hold the PAN@COF-SCU1 nanofibers. Then the PAN@COF-SCU1 nanofibers packed cartridge was conditioned sequentially with 1.0 mL of methanol and 1.0 mL of ultrapure water. Subsequently, 6.0 mL sample extract was allowed to pass through the PAN@COF-SCU1 nanofibers packed PT-SPE cartridges. After that, the cartridges were washed with 0.5 mL ultrapure water and the retained analytes in the PAN@COF-SCU1 nanofibers were eluted with 2 mL of 20% ammonia–methanol (V:V), and the eluate was concentrated to dryness using a mild stream of nitrogen. Finally, the residues were analyzed by HPLC after redissolving in 0.2 mL of mobile phase.

3. Results and discussions

3.1 Characterization of COF-SCU1 and PAN@COF-SCU1 nanofibers

The SEM image of as-synthesized COF-SCU1 (Fig. 2a) showed that the particles were seriously agglomerated after being dried, and the particle size of individual one was smaller than 100 nm. Nevertheless, the as-synthesized COF-SCU1 before drying showed good dispersity because of its small particle size and light density (Fig. S1 in supporting information), which was beneficial for obtaining a homogeneous electrospining solution with matrix for further electrospun nanofibers preparation. The functional groups information of COF-SCU1 was characterized by FT-IR (Fig. 2b).

The characteristic band at 2853 cm^{-1} was corresponding to the C-H vibration of the aromatic rings. The band at 1713 cm^{-1} was ascribed to the C=O stretching of carboxylic groups. While the characteristic band at around 1658 cm^{-1} was attributed to the stretching of amide, which confirmed that COF-SCU1 was built up by forming amide bond between p-phenylenediamine and trimesoyl chloride. The XRD pattern of COF-SCU1 (Fig. 2c) with a single broad diffraction peak at 25.3° revealed that its structure was basically amorphous. Nitrogen adsorption-desorption isotherm was performed to test the porosity of COF-SCU1 (Fig. 2d). It was determined that the Brunauer-Emmett-Teller (BET) surface area, Barrett-Joyner-Halenda (BJH) adsorption average pore width and total pore volume were 45.6 m^2 g^{-1}, 25.6 nm and 0.29 m^3 g^{-1}, respectively. The zeta potentials of COF-SCU1 were measured in the pH range of 2-11 (Fig. 2e). It was clearly found that COF-SCU1 was negatively charged in the pH range of 2-11, and the surface charge became more negative as the pH increased from 2 to 11 due to the deprotonation of the carboxylic groups. TGA analysis was performed to examine the thermal stability of COF-SCU1 (Fig. 2f). The result showed that COF-SCU1 exhibited good thermal stability up to 300 ℃. In order to evaluate the chemical stability, COF-SCU1 was immersed in methanol, 10 mM NaOH and 10 mM HCl for 48 h, respectively. It was found that the FT-IR spectra and XRD pattern of COF-SCU1 in these solvents coincided well with that of the fresh one (Fig. S2 in supporting information), which indicated the good chemical stability of COF-SCU1.

In this study, the electrospun nanofibers were utilized as substrate materials to fabricate COFs-incorporated nanofibers. As can be seen from Fig. 3a, the uniform three dimensional networks of PAN electrospun nanofibers make it a suitable substrate to fabricate COFs incorporated nanofibers. The SEM results of the prepared PAN@COF-SCU1 nanofibers in Fig. 2 showed that the problem of serious agglomeration of COF-SCU1 was effectively avoided. It was also found that the loading ratios of COF-SCU1 significantly affected the morphologies of the resultant nanofibers. As the loading ratio of COF-SCU1 was 10%, relatively uniform nanofibers with few beads could be obtained. As the loading ratios of COF-SCU1 increased from 10 to 30%, more beads would existed in the prepared nanofibers. Furthermore, it could be seen that the surface of the PAN@COF-SCU1 nanofibers became smooth compared to that of PAN nanofibers. The TEM result of PAN@COF-SCU1 nanofibers confirmed that relatively uniform nanofibers without serious agglomeration of COF-SCU1 could be obtained (Fig. S3 in supporting information). The chemical structure of the prepared PAN@COF-SCU1 nanofibers were analyzed by FT-IR (Fig. S4 in supporting information). The characteristics bands of COF-SCU1 and PAN, such as bands at 1713 and 1658 cm^{-1} of COF-SCU1 and band at 2242 cm^{-1} of PAN, could be observed in the spectrum of the PAN@COF-SCU1 nanofibers, showing that COF-SCU1 remained intact after electrospinning. In addition, the XRD result of the PAN@COF-SCU1 nanofibers showed that PAN@COF-SCU1 nanofibers were amorphous due to the amorphous structure of both PAN and COF-SCU1 (Fig. S5 in supporting information).

3.2 Optimization of PT-SPE

3.2.1 Effect of loading ratios of COF-SCU1

The effect of loading ratios of COF-SCU1 in the PAN@COF-SCU1 nanofibers was firstly evaluated. As listed in Fig. 4a, the recoveries of TCs were below 10% when pure PAN nanofibers was utilized as adsorbents, showing the poor adsorption efficiency of PAN nanofibers towards the tested TCs. Nevertheless, the recoveries of TCs increased steadily as the loading ratios of COF-SCU1 increased from 0 to 30%, and the recoveries of TCs were in the range of 84-99% when the loading ratio of COF-SCU1 was 30%. The above results demonstrated that COF-SCU1 in the nanofibers was dominant in the adsorption of TCs. In addition, PAN@COF-SCU1 (0.3) nanofibers was selected as adsorbents for the extraction of TCs.

3.2.2 Effect of amount of PAN@COF-SCU1 nanofibers

To ensure the satisfied recoveries of TCs, the amount of PAN@COF-SCU1 nanofibers were optimized in the range of 2-12 mg (Fig. 4b). It was found that the recoveries of TCs improved from 8.4-12.6% to 82.8-95.1% as the amounts of PAN@COF-SCU1 nanofibers increased from 2 to 10 mg. Nevertheless, further increasing the amounts of PAN@COF-SCU1 nanofibers from 10 to 12 mg could lead to the decreased recoveries of TCs. Therefore, PT-SPE cartridges packed with 10 mg PAN@COF-SCU1 nanofibers were used in the following experiments.

3.2.3 Effect of pH value of sample solution

The pH value of sample solution is of vital importance in the extraction of analytes because it can affect the existing forms of TCs and the charge species of the adsorbent. In this work, the effect of pH value of sample solution on the recoveries of TCs was carried out in the pH range of 3-11. As shown in Fig. 4c, the recoveries of TCs improved at different level with increasing pH from 3 to 7, then decreased obviously with further increasing pH from 7 to 11. According to the chemical structures and pK_a values of TCs (Table S1, in supporting information), TCs would exist in cationic forms at pH 3, and the possible adsorption mechanisms between TCs and PAN@COF-SCU1 nanofibers would be electrostatic interaction, hydrogen interaction and π-π interaction between the positively charged TCs and the negatively charged COF-SCU1 in the nanofibers. As the pH values in the range of 4-7, TCs would exist in intermediate forms, and the enhanced recoveries of TCs should be attributed to the considerable hydrophobic interaction between TCs and COF-SCU1 in the nanofibers. The existing forms of TCs would swift from intermediate forms to anionic forms as the pH value increased from 7 to 11. However, the anionic forms of TCs could not be effectively adsorbed on PAN@COF-SCU1 nanofibers because of the electrostatic repulsion between TCs and the negatively charged COF-SCU1 in the nanofibers. Based on the results, the pH value of sample solution was adjusted at pH 7 in the following experiments.

3.2.4 Effect of desorption solvent

It is important to use a reasonable desorption solvent to desorb analytes from adsorbent and thus obtain satisfied recoveries of analytes. Considering that basic conditions was not beneficial for the adsorption of TCs on PAN@COF-SCU1 nanofibers, methanol, acetonitrile, 5% ammonia-methanol and 5% ammonia-acetonitrile were firstly studied to desorb the TCs from PAN@COF-SCU1 nanofibers. As shown in Fig. 4d, it was clearly that alkaline methanol solution showed the best desorption efficiencies among the four desorption solvents. To further improve the desorption efficiencies, the ammonia content in the alkaline methanol was optimized in the ranged from 5 to 25% (Fig. 4e). The recoveries of TC improved gradually with increasing the ammonia content from 5 to 25%, and the recoveries of OTC and CTC would be the highest when the content of ammonia was 20%. Thus, 20% ammonia-methanol was selected as the desorption solvent. Finally, the volume of desorption solvent ranged from 0.5 to 2.5 mL was also evaluated. As shown in Fig. 4f, it indicated that 2.0 mL 20% ammonia-methanol was sufficient to desorb the TCs from PAN@COF-SCU1 nanofibers.

3.3 Method validation

Under the optimized condition, the relevant performance of the developed PT-SPE/HPLC method for the determination of TCs including the linear range, precision, the limits of quantification (LOQ) based on a signal-to-noise (S/N) ratio of 10 and the limits of detection (LOD) based on a signal-to-noise (S/N) ratio were validated, and the results were summarized in Table 1. The linear range of the three TCs was in the range of 4-70 ng mL^{-1} with good correlation coefficient ($R^2 \geq 0.998$). The LOQs and LODs were in the range of 2-10 ng mL^{-1} and 0.6-3 ng mL^{-1}, respectively. The interday and intraday precisions (RSD, %) based on five replicated experiments at the spiked concentration of 50 ng mL^{-1} were determined to be 4.57-8.46%, indicating the high reliability and reproducibility of the proposed method[3, 5, 33-36]. The analytical performance of the proposed method was compared with those of other reported methods for the determination of TCs, and the results were shown in Table 2. It was worthy to mention that the proposed method showed low LODs for TCs using fewer sample consumption compared with the listed methods.

3.4 Reproducibility and reusability of PAN@COF-SCU1 nanofibers

The reproducibility and reusability are one of the important indicators of adsorbents. In this work, the reproducibility was investigated by three different batches of PAN@COF-SCU1 nanofibers. The reusability of PAN@COF-SCU1 nanofibers was verified by five consecutive cycles of PT-SPE operation, and the used PT-SPE cartridges were rinsed sequentially by 2.0 mL methanol and 2.0 mL pure water prior to next PT-SPE operation. The results showed that the RSD values of recoveries of TCs in the batch-to-batch reproducibility were less than 10% (Table S2, in supporting information), and the recoveries of TCs decreased less than 30% after five consecutive cycles of PT-SPE operation (Fig. S6 in supporting information). The above results demonstrated that the PAN@COF-SCU1 nanofibers exhibited acceptable reproducibility and reusability.

3.4 Real sample analysis

The proposed method was applied to the analysis of the TCs in grass carp and duck samples, respectively. The recoveries and RSDs of TCs for the analysis of grass carp and duck samples were calculated by determining spiked concentrations of TCs at 10, 30 and 50 ng mL^{-1}, respectively. As shown in Table 3, the recoveries of three TCs in duck ranged from 84.02 to 113.5% with the RSDs less than 9.5%, and the recoveries of TCs in grass carp was in the range of 82.74-117.5% with the RSDs less than 9.0%. The typical HPLC-PDA chromatograms of real samples before PT-SPE, real samples after PT-SPE, spiked real samples before PT-SPE and spiked real samples after PT-SPE were shown in Fig. 5. It could be clearly found that the peak high of the target TCs in the spiked real samples increased significantly after PT-SPE procedure, demonstrating that the PAN@COF-SCU1 nanofibers exhibited good performance toward the enrichment of TCs in grass carp and duck samples. The results indicated that the developed PT-SPE/HPLC method using PAN@COF-SCU1 nanofibers as adsorbent could be used for the effective attraction and analysis of TCs in duck and grass carp samples.

4. Conclusion

In summary, a novel PAN@COF-SCU1 nanofibers were fabricated via a facile electrospinning method and utilized as adsorbent in PT-SPE for the extraction of TCs, and the proposed PT-SPE/HPLC method was successfully used for the extraction and analysis of TCs in grass carp and duck samples. The PAN@COF-SCU1 nanofibers exhibited high extraction efficiencies toward TCs based on multiple mechanisms, such as electrostatic interaction, hydrogen interaction, hydrophobic interaction and π-π interaction between TCs and COF-SCU1 in nanofibers. The established PT-SPE/HPLC method for the analysis of TCs showed good analytical performance, which was successfully used for the analysis of TCs in grass carp and duck samples with high recoveries and precisions.

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Figure captions

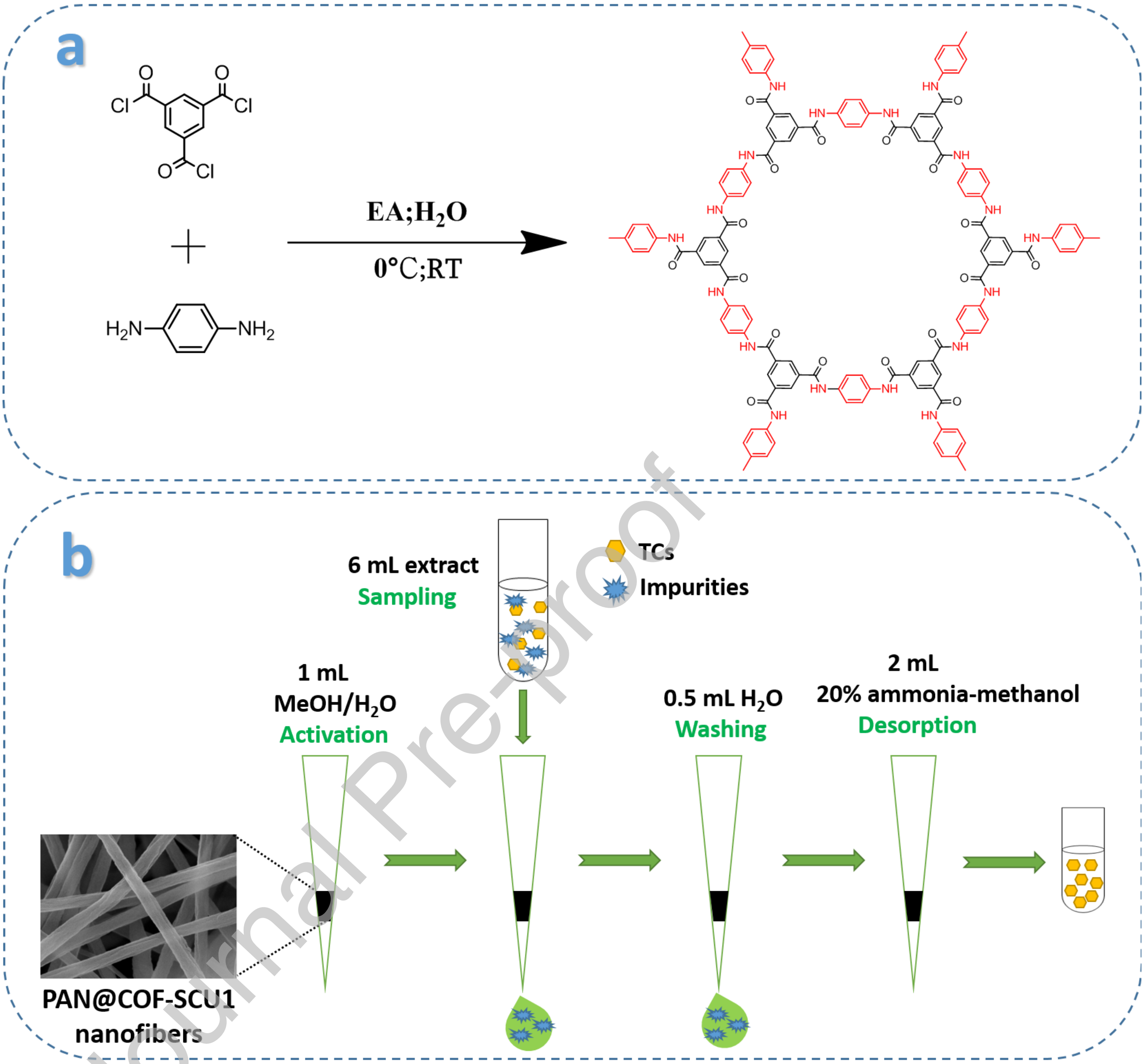

Fig. 1 Schematic diagrams of (a) preparation of COF-SCU1 and (b) PT-SPE procedure for the extraction of TCs.

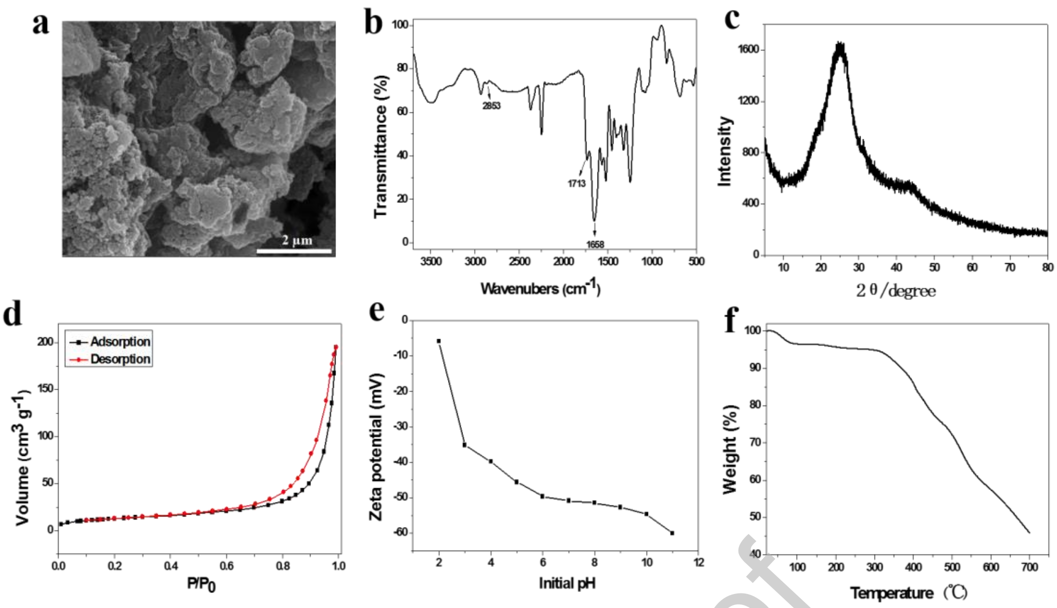

Fig. 2 (a) SEM image of COF-SCU1; (b) FT-IR spectra of COF-SCU1; (c) XRD pattern of COF-SCU1; (d) Nitrogen adsorption and desorption isotherms of COF-SCU1; (e) Zeta potential of COF-SCU1; (f) TGA analysis of COF-SCU1.

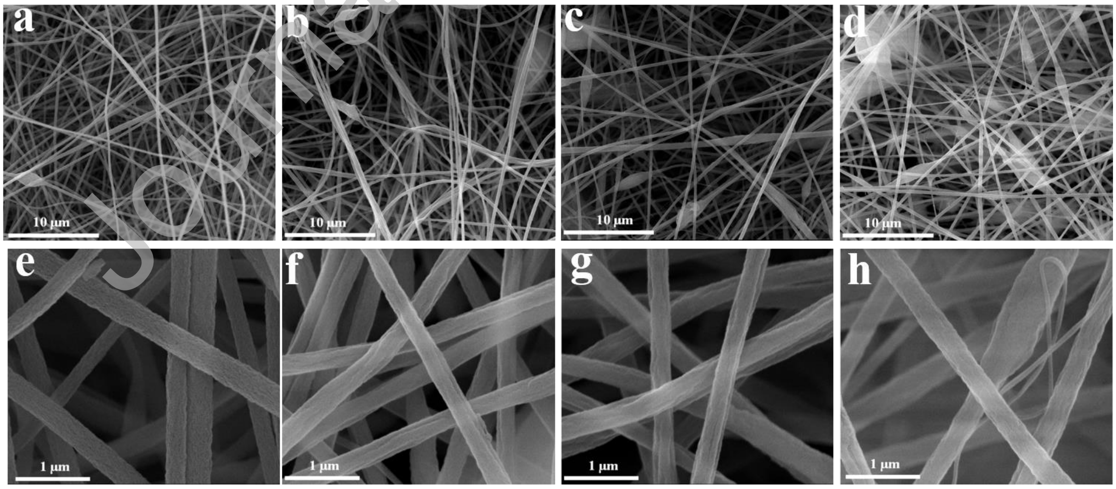

Fig. 3 SEM images of PAN nanofibers (a and e); PAN@COF-SCU1 (0.1) (b and f); PAN@COF-SCU1 (0.2) (c and g); PAN@COF-SCU1 (0.3) (d and h) .

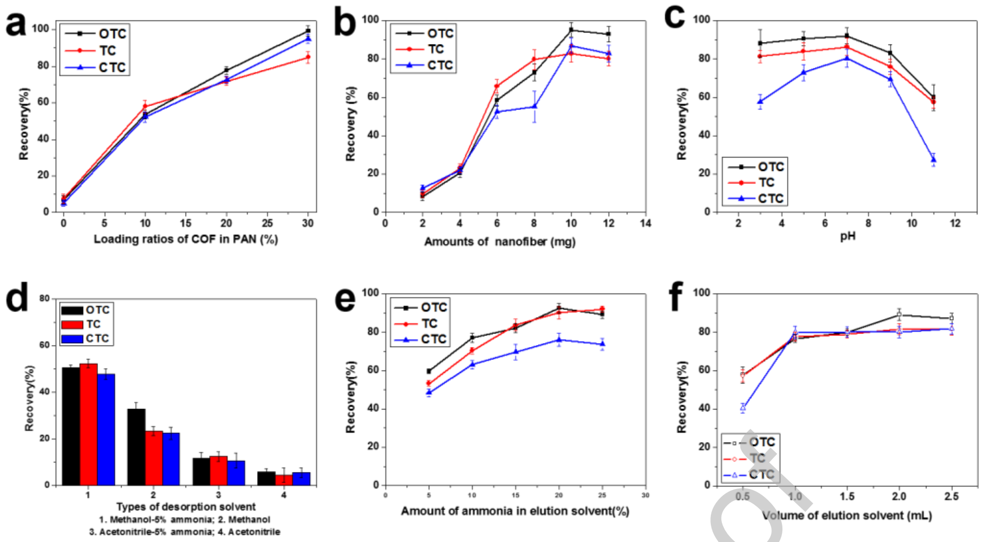

Fig. 4 (a) Effect of loading ratios of COF-SCU1; (b) Effect of amounts of PAN@COF-SCU1 nanofibers; (c) Effect of matrix pH; (d): Effect of different types of elution solvent; (e) Effect of ammonia content in elution solvent; (f) Effect of volume of elution solvent.

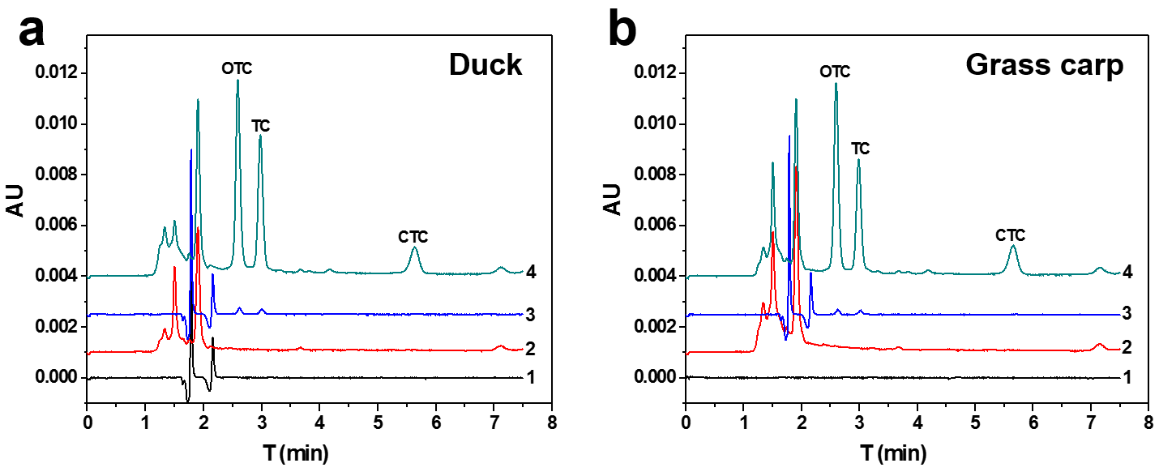

Fig. 5 (a) Typical HPLC chromatograms of (1) duck sample; (2) duck sample after PT-SPE; (3) duck sample spiked with 50 ng mL^{-1} before PT-SPE; (4) duck sample sample spiked 50 ng mL^{-1} after PT-SPE. (b) Typical HPLC chromatograms of (1) grass carp sample; (2) grass carp sample after PT-SPE; (3) grass carp sample spiked with 50 ng mL^{-1} before PT-SPE; (4) grass carp sample sample spiked 50 ng mL^{-1} after PT-SPE.

Table 1. Characteristic data for the PT-SPE with PAN@COF-SCU1 nanofiber as sorbent for HPLC determination of TCs.

Analytes	Linear range (ng mL^{-1})	R^2	LOD (ng mL^{-1})	LOQ (ng mL^{-1})	RSD(%) (70 ng m
					Intra-day
OTC	4-70	0.9989	0.6	2	4.57
TC	4-70	0.9999	0.6	2	8.46
CTC	10-70	0.9980	3	10	5.97

Table 2. Comparison of the different methods for the determination of TCs.

Sorbent	Method	Sample	Amount of sorbent (mg)	Elution volume (mL)	(
ZIF-8	Online-SPE/HPLC	Water, milke	-	1	
MIP	SPE /HPLC	Milk, egg, pork	30	1	
Oasis HLB	SPE /HPLC	Bovine milk	200	5	
Discovery DSC-phenyl	SPE /HPLC	Honey	500	5	
Graphene	SPE /HPLC	Milk	10	2	
CTPCC-TP	SPE /HPLC	Egg, chicken, et. al	60	5	
PAN@COF-SCU1	PT-SPE/HPLC	Duck, grass carp	10	2	

CTP_{CC-CP}:covalent triazine-terphenyl polymer; MIP: Molecular Imprinted Polymer.

Table 3. Analytical results for the determination of TCs in duck and Grass carp samples.

Analytes	Added (ng mL^{-1})	Duck			Grass carp	
		Found (ng mL^{-1})	Recovery (%)	RSD (%)	Found (ng mL^{-1})	Recove (%)
OTC	10	11.35	113.5	2.8	11.33	113.
	30	30.59	101.97	4.9	31.66	105.5
	50	55.35	110.7	9.5	54.53	109.0
TC	10	10.24	102.4	5.9	10.3	103.
	30	26.95	89.83	6.5	25.41	84.7
	50	48.55	97.1	5.2	41.37	82.7
CTC	10	11.04	110.4	1.2	11.75	117.
	30	25.21	84.03	6.2	29.1	97.0
	50	50.59	101.18	4.7	55.31	110.6

Credit Author Statement

Ronglin Wang: Designed and participated the experiment, Writing-Original draft preparation. Zhiming Yan: Designed the experiment and revised the manuscript and was responsible for the supervision of the whole research. Canru Li and Qianlian Li: participated in the experiment and revision of the paper. Sunxian Zhang: participated in the experiment and analysis the experimental date. Feng lv: Writing- Reviewing and was responsible for the supervision of the whole research.

Conflict of Interest Statement

We wish to draw the attention of the editor to the following facts which may be considered as potential conflicts of interest and to significant financial contributions to this work.

We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

We confirm that we have given due consideration to the protection of intellectual property associated with this work and there are no impediments to publication, including the timing of publication the regulations of our institutions concerning intellectual property.