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# Covalent organic framework-sodium alginate-Ca<sup>2+</sup>-polyacrylic acid composite beads for convenient dispersive solid-phase extraction of neonicotinoid insecticides in fruit and vegetables



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#### ABSTRACT

Neonicotinoids, the fastest-growing class of insecticides, have posed a multi-media residue problem with adverse effects on environment, biodiversity and human health. Herein, covalent organic framework-sodium alginate-Ca<sup>2+</sup>-polyacrylic acid composite beads (CACPs), facilely prepared at room temperature, were used in convenient dispersive solid-phase extraction (dSPE) and combined with high-performance liquid chromatography (HPLC) for the detection of five neonicotinoid insecticides (thiamethoxam, acetamiprid, dinotefuran, clothianidin, imidacloprid). CACPs can be completely separated within 1 min without centrifugation. After seven adsorption/ desorption cycles, it maintained high extraction efficiencies (>90%). The developed method exhibited a wide linear range (0.01  $\sim$  10  $\mu$ g mL<sup>-1</sup>), low limits of detection (LODs, 0.0028  $\sim$  0.0031 mg kg<sup>-1</sup>), and good repeatability (RSD  $\leq$  8.11%, n = 3). Moreover, it was applied to the determination of five neonicotinoids in fruit and vegetables (peach, pear, lettuce, cucumber, tomato), and recoveries ranged from 73.6% to 116.2%.

### 1. Introduction

Neonicotinoids are the fastest-growing insecticides of the five major chemical classes in the world (Klingelhöfer et al., 2022). Due to their ubiquitous presence, high polarity and good water solubility, neonicotinoids are easily taken up by plant tissues and result in long-term residual, and have been commonly found in fruit and vegetables at concentrations of  $0.004 \sim 0.5 \text{ mg kg}^{-1}$  (Wang et al., 2022). The widespread use and multi-media residue of neonicotinoids and the resulting decline of biodiversity are now of global concern. Moreover, neonicotinoid exposure presents potential hazards to mammals and even humans, involving neurotoxicity, immunotoxicity, genetic toxicity and reproductive toxicity (Han et al., 2018). The European Union (EU) and China have established maximum residue limits (MRLs) for neonicotinoids in fruit and vegetables ( $0.01 \sim 20 \text{ mg kg}^{-1}$ ). Therefore, determining trace neonicotinoid residue in fruit and vegetables is essential for safeguarding food safety and human health.

Various techniques have been reported for the determination of neonicotinoid pesticides, such as fluorescence, immunoassay, electrochemistry and chromatography (Wang et al., 2022). Considering that neonicotinoids have a low volatility and a high polarity ( $\log Kow = -1.16$  $\sim$  0.62), high performance liquid chromatography (HPLC) was mainly applied to realize the detection and analysis of neonicotinoids (Watanabe, 2021). The trace level of neonicotinoid residue, along with the complex sample matrix, makes it indispensable to establish an efficient pretreatment method before HPLC analysis. Currently, solid-phase extraction (SPE) (Zhang et al., 2016), quick, easy, cheap, effective, rugged, and safe (QuEChERS) (Zhao & Shi, 2022), magnetic solid-phase extraction (MSPE) (Li et al., 2022) and dispersive solid-phase extraction (dSPE) (Cao et al., 2018) have been reported for analyzing neonicotinoids. Among these methods, dSPE has gained widespread attention because of its high flexibility and satisfactory recoveries, in which the adsorbent acts as a vital factor for its efficiency.

Functionalized nanomaterials with different morphologies and

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compositions, such as metal-organic frameworks (MOFs), porous organic polymers (POPs) and covalent organic frameworks (COFs) have been successfully applied in dSPE (Büyüktiryaki et al., 2020). COFs have great potential to be applied in dSPE owing to their large surface area, adjustable pore size and good thermal stability (Zhi et al., 2020). In particular, room-temperature synthesis method has the advantages of simplicity, high efficiency, mild conditions, energy saving, and environmental protection. Due to the nanometer size range and low density, separation of COFs (adsorbents) during dSPE process is time-consuming and energy-consuming (Romero et al., 2022, Pezhhanfar et al., 2023). It is also difficult to achieve complete separation, which is detrimental to the recycling of adsorbents and leads to possible secondary environmental pollution. Magnetic COFs, such as EB-COF@Fe<sub>3</sub>O<sub>4</sub> (Li et al., 2022) and magnetic COF-DtTb (Lin et al., 2020), have been synthesized for convenient dSPE, avoiding high-speed centrifugation. It is energyconsuming to provide a corresponding strong magnetic field in largescale applications. Preparing COFs-based materials that can be easily and quickly separated without additional magnetic fields or centrifugal procedures is necessary. In addition, most of the reported COFs are hydrophobic, limiting their application in the adsorption of polar analytes (Li et al., 2018).

Alginate is a hydrophilic polysaccharide abundant in hydroxyl and carboxyl groups. It can interact with  $Ca^{2+}$  to form a hydrogel by the chain-chain association, which is environmentally friendly, easy to prepare, non-toxic, biocompatible and biodegradable. Incorporating COFs into alginate- $Ca^{2+}$  hydrogel has the potential to be applied in dSPE to simplify the separation process of adsorbents in conventional dSPE, as well as realize the effective adsorption of organic pollutants, especially polar organic pollutants.

In this work, COF TAPB-DMTA was synthesized at room temperature and composited with hydrophilic sodium alginate to prepare hydrogel, named COF-sodium alginate- $Ca^{2+}$ -polyacrylic acid composite beads (CACPs), which were used as adsorbents to realize convenient dSPE of polar neonicotinoids. Combined with HPLC, CACPs-dSPE was successfully applied to simultaneous determination of five neonicotinoids (dinotefuran, clothianidin, imidacloprid, thiamethoxam, acetamiprid) in fruit and vegetable samples (peach, pear, lettuce, cucumber, tomato).

## 2. Materials and methods

### 2.1. Chemicals

All chemicals were at least analytical grade and used without further purification. 1, 3, 5-tris-(4-aminophenyl) benzene (TAPB), 2, 5-dimethoxyterephthalaldehyde (DMTA) were purchased from Shanghai Haohong Biomedical Science and Technology Co., Ltd. (Shanghai, China). Polyacrylic acid (PAA) was taken from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). Calcium chloride (CaCl<sub>2</sub>), sodium alginate, ammonia, acetic acid, acetone, acetonitrile, methanol, 1, 4-dioxane, 1, 3, 5-trimethylbenzene were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Acetamiprid (99.9%) and clothianidin (98.9%) were obtained from ANPEL Laboratory Technologies Co., Ltd. (Shanghai, China). Dinotefuran (96%), imidacloprid ( $\geq$ 97%), and thiamethoxam (95%) were acquired from Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China).

#### 2.2. Apparatus and instruments

The surface morphology of COF TAPB-DMTA, sodium alginate-Ca<sup>2+</sup>polyacrylic acid composite beads (ACPs) and CACPs were observed by scanning electron microscope (SEM) (SU8100, Hitachi, Japan). The chemical groups and elements of the synthesized COF, ACPs and CACPs were characterized by Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific IN10, USA) and K-Alpha X-ray photoelectron spectrometer (XPS, Thermo Scientific, USA). The D8 Force advance diffractometer (Bruker, Germany) was used to record X-ray diffraction (XRD) patterns. The nitrogen adsorption/desorption experiments were conducted using a gas sorption analyzer (Autosorb-IQ, Quantachrome, USA). The Alpha 1-2 LDplus Freeze Dryer (Martin Christ Freeze Dryers, Germany) was used to freeze-dry ACPs and CACPs. An STA 449 F5 Jupiter thermal gravimetric analyzer (NETZSCH, Germany) was employed to perform the thermogravimetric analysis (TGA).

The chromatographic analysis was conducted using a Waters e2695 HPLC-DAD system (Milford, USA) and a Waters XBridge® C18 (5  $\mu$ m, 4.6  $\times$  250 mm) column. The mobile phase was acetonitrile and water (25:75, v:v) with a flow rate of 1 mL min^{-1}. The column temperature was maintained at 25°C. Detection wavelengths were set at 270 nm for dinotefuran, clothianidin and imidacloprid, 246 nm for acetamiprid and 253 nm for thiamethoxam.

## 2.3. Synthesis of COF TAPB-DMTA

COF TAPB-DMTA was synthesized by a facile room-temperature method (Liu et al., 2019). Briefly, TAPB (112.46 mg, 0.32 mmol) and DMTA (93.20 mg, 0.48 mmol) were mixed into a 25 mL bottle, with an addition of 3 mL mesitylene and 3 mL 1,4-dioxane. Then the acetic acid (3 mol/L, 1 mL) was added after sonicating for 20 min. The reactants were stirred for 72 h at room temperature and the obtained precipitate was washed with methanol three times to remove excess impurities (9500 r min<sup>-1</sup>, 10 min). After drying for 24 h in a vacuum oven at 60°C, the obtained COF TPB-DMTP was ground into powder to prepare CACPs.

## 2.4. Preparation of CACPs

The preparation of CACPs was referred to Yang, S et al. (Yang et al., 2020) in the preparation of MOF-polymer composite beads with modifications. The synthesis process was optimized as follows (Fig. 1B, Video 1). 25 mg mL<sup>-1</sup> of TAPB-DMTA was mixed with 20 wt% sodium alginate solution and sonicated to form a homogeneous suspension. Meanwhile, 120 mg CaCl<sub>2</sub> was dissolved in 20 mL of 0.01 mol/L PAA solution to prepare curing solution. The COF-sodium alginate suspension was dropwise added to curing solution, and magnetic stirring was assisted to make complete curing. The beads were collected after shaping and washed with ultrapure water. After freeze-drying for 24 h, CACPs with a diameter of 4  $\sim$  5 mm were obtained.

## 2.5. Real samples preparation and dSPE procedure

Lettuce, cucumber, tomato, peach, and pear samples were bought from a local market (Wuxi, Jiangsu, China), washed and cut into small pieces for homogenization. Homogenized samples (100 g) were centrifuged (8000 r min<sup>-1</sup>, 10 min) to collect the supernatant. Filtered through 0.22  $\mu$ m aqueous filter membrane, the sample solutions were obtained and stored at 4°C before dSPE. A 10-fold dilution was made at dSPE.

The dSPE procedure is illustrated in Fig. 1C. Adding 18 of CACPs to the sample solution (10 mL), ultrasonic-assisted extraction was carried out (40 min). Then the supernatant was aspirated with a pipette, CACPs were taken out using tweezers and placed on the absorbent paper to dispose of the residual solution on the surface. The CACPs were subsequently placed into the centrifuge tube (5 mL) and eluted with methanol (0.5 mL, 15 min). The eluate was filtered through a 0.22  $\mu$ m nylon filter for HPLC-DAD analysis.

## 2.6. Method validation and statistical analysis

The developed CACPs-dSPE-HPLC method was evaluated by linearity, limit of quantification (LOQs, S/N = 10), limit of detection (LODs, S/N = 3), recovery, and relative standard deviation (RSD). Besides, the matrix effects on detecting trace neonicotinoid insecticides in fruit and vegetables (peach, pear, lettuce, cucumber, tomato) were also validated. The matrix effects values (%ME) were calculated using the following



Fig. 1. Schematic diagram of (A) synthesis of COF TAPB-DMTA, (B) preparation of CACPs, and (C) dSPE operational procedures.

equation (Pano-Farias et al., 2017):

$$ME\% = \left[1 - \left(\frac{Slope_{solution}}{Slope_{matrix-matched}}\right)\right] \times 100\%$$

where Slope<sub>solution</sub> represents the slope of the solution calibration curve, Slope<sub>matrix-matched</sub> represents the slope of the matrix-matched calibration curve.

Statistical analysis was accomplished by Origin 2021 (OriginLab Software, Northampton, MA, USA) and Excel (Microsoft).

#### 3. Results and discussion

#### 3.1. The design of CACPs for dSPE of neonicotinoids

Neonicotinoids are polar molecules with low octanol/water partition coefficient (LogKow = -1.16  $\sim$  0.62) (Li et al., 2022), having a conjugated system formed by nitro/nitrile and guanidine/amidine group. The molecular size of neonicotinoids is in the range of 10.2  $\sim$  13.6 Å (Fig. S11). The COF-based composite beads (CACPs) were prepared for dSPE of neonicotinoids (Fig. 1, Fig. S1). Specifically, the imine-bonded COF TAPB-DMTA is a large  $\pi$ -conjugated system with a uniform pore size of about 3.012 nm. Enhancing the hydrophilicity of TAPB-DMTA could potentially facilitate its adsorption of polar neonicotinoids, thus it was composited with sodium alginate, which is a hydrophilic polysaccharide abundant in hydroxyl and carboxyl groups. Meanwhile, sodium alginate could interact with Ca<sup>2+</sup> to form a hydrogel, making it possible to simplify the separation operation and shorten the separation time of the adsorbents in the dSPE process. In summary, CACPs were prepared and used as adsorbents for effective and convenient dSPE of neonicotinoids. Coupled with HPLC-DAD, CACPs-dSPE was used for determining five neonicotinoids (dinotefuran, clothianidin, imidacloprid, thiamethoxam, acetamiprid) in fruit and vegetable samples (peach, pear, lettuce, cucumber, tomato).

## 3.2. Optimization of preparation conditions for CACPs

The CACP is a cross-linked network structure composed of alginate,

 $Ca^{2+}$ , PAA and TAPB-DMTA. To prepare CACPs with more stable structures and better extraction performances, the concentration of  $Ca^{2+}$ , PAA and TAPB-DMTA and the size of CACPs were investigated.

## 3.2.1. Effect of the concentration of $Ca^{2+}$

The selective and synergistic binding of  $Ca^{2+}$  and sodium alginate determines the gelation and mechanical rigidity of CACPs, which is owing to the cage-like structure formed by the interaction between  $Ca^{2+}$  and acidic sites on the G residues (Hecht & Srebnik, 2016). To summarize, the concentration of  $Ca^{2+}$  influences the reticulation, stability, and adsorption properties of CACPs, so it was optimized. As evident from Fig. S2A, the peak areas of five neonicotinoids were larger overall at a  $Ca^{2+}$  concentration of 6 mg mL<sup>-1</sup>. Furthermore, at 3 mg mL<sup>-1</sup>, the structure of the CACPs was loose and slightly dissociated when dispersed in aqueous solution, which was unfavorable for dSPE and regeneration. Contrariwise, at 9 mg mL<sup>-1</sup>, the structure of the CACPs was tight, which might be negative for the adsorption of the analytes. Therefore, 6 mg mL<sup>-1</sup>  $Ca^{2+}$  was used to prepare CACPs in subsequent experiments.

#### 3.2.2. Effect of the concentration of PAA

Adding PAA can strengthen the cross-link between alginate chains and  $Ca^{2+}$ , and also introduce ionic interactions and hydrogen bonds between PAA-PAA, PAA- $Ca^{2+}$  and PAA-alginate (Cho et al., 2019), thus improving the stability of the composite beads and their utility in dSPE (Yang et al., 2020). Consequently, the concentration of PAA was optimized (Fig. S2B). The peak areas of acetamiprid, imidacloprid and clothianidin were larger at a PAA concentration of 0.005 mol/L, while the peak areas of dinotefuran and thiamethoxam were larger at 0.01 mol/L. As the concentration of PAA continued to increase, the peak areas of five neonicotinoid insecticides then decreased, which could be attributed to the diffusion of the polymer into the COF pores during the gelation process, occupying the adsorption sites of COF for the analytes. Considering that the peak areas of dinotefuran and thiamethoxam were much lower in comparison, 0.01 mol/L of PAA was selected to keep the peak areas of all analytes at a relatively higher level.



Fig. 2. The SEM images of (A, B) TAPB-DMTA, (C, D) ACPs and (E, F) CACPs. (G) FI-IR spectra, (H) TGA curve and (I) XPS survey spectra of CACPs.

#### 3.2.3. Effect of the size of CACPs

To assess the influence of CACP size, different sizes of CACPs were prepared with varying sizes of pipette tips. Using the same mass of CACPs for dSPE, the results (Fig. S2C) showed the peak areas were larger overall when extracted using CACPs prepared with 1 mL pipette tips.

#### 3.2.4. Effect of the concentration of TAPB-DMTA

COF TAPB-DMTA could provide active sites to adsorb neonicotinoid insecticides, thus the content of TAPB-DMTA was optimized (Fig. S2D). The peak areas increased significantly with the increasing amount of TAPB-DMTA in the range of  $5 \sim 50 \text{ mg mL}^{-1}$ . However,  $50 \text{ mg mL}^{-1}$  of COF powder was poorly dispersed in sodium alginate solution, so the content of COF was selected to be 25 mg mL<sup>-1</sup> for comprehensive consideration.

#### 3.3. Characterization of COF TAPB-DMTA and CACPs

The structural integrity and phase purity of TAPB-DMTA were verified by XRD. As displayed in Fig. S3, the strongest characteristic diffraction peaks at 2.80° corresponded to the (100) planes, and a broad peak at 25.3° corresponded to the (001) plane. Additionally, the diffraction peaks at 4.82°, 5.57°, 7.39° and 9.68° were attributed to (110), (200), (210) and (220) planes, respectively. The results were consistent with the previous report (Zhang et al., 2018). The micromorphology of TAPB DMTA, sodium alginate-Ca<sup>2+</sup>-polyacrylic acid composite beads (ACP) and CACPs were characterized by SEM. TAPB-DMTA (Fig. 2A, B) presented a spherical structure with a diameter of about 2 ~ 3  $\mu$ m, which generally agreed with the reported results (Ma et al., 2019). ACPs (Fig. 2C, D) and CACPs (Fig. 2E, F and Fig. S4) presented a lamellar structure with porous cavities, which could be attributed to the constrained motion of alginate polymer in high-viscosity alginate solution (Daradmare et al., 2021). For the internal

structures of CACPs, the spherical structure similar to TAPB-DMTA could be observed in the porous structure, initially proving that TAPB-DMTA had been successfully loaded.

The FTIR spectra of TAPB-DMTP (Fig. S5) showed that the characteristic peak of C=N appeared at 1611 cm<sup>-1</sup>, accompanied by a decrease in the C=O stretching vibration (1677  $cm^{-1}$ ) of DMTP and N-H stretching vibration  $(3300 \sim 3100 \text{ cm}^{-1})$  of TAPB, providing persuasive proof for the covalent conjugation of TAPB and DMTA (Zhang et al., 2018). For CACPs (Fig. 2G), the characteristic peaks at 1710  $\text{cm}^{-1}$  and 1592  $\text{cm}^{-1}$  corresponded to the asymmetric and symmetric C=O stretching vibration associated with the carboxylic acid group respectively (Daradmare et al., 2021), and the peak at 1026 cm<sup>-1</sup> corresponded to the C-O-C stretching in ACPs (Lee et al., 2020). The characteristic peaks of TAPB-DMTA and ACPs were seen in CACPs, demonstrating the successful preparation of composite beads. Furthermore, the C=O stretching band of carboxylic acid group was slightly shifted towards lower wavelengths, confirming the strong interaction between carboxyl/hydroxyl groups of sodium alginate and aldehyde/amino functionalities in TAPB-DMTA (Daradmare et al., 2021).

The thermal stability was characterized by TGA (Fig. 2H). It revealed that TAPB-DMTA was stable below 412°C, and ACPs and CACPs were stable below 210°C, which signified that the ACPs and CACPs had good thermal resistance. In addition, CACPs had less mass loss than ACPs at 210°C, demonstrating that the addition of TAPB-DMTA had improved the thermal resistance of the composite beads. The permanent porosity of CACPs was evaluated by N<sub>2</sub> adsorption–desorption isotherm (Fig. S6). CACPs had a Brunauer-Emmett-Teller (BET) surface area of 122.262 m<sup>2</sup> g<sup>-1</sup> and pore size of 2.531 nm, which adhered to a type IV(a) isotherm, indicating their mesoporous nature.

XPS of CACPs (Fig. 2I) verified the existence of C, N, O, Na and Ca in CACPs. The high-resolution XPS spectra of C 1 s (Fig. S7A) showed three peaks at 284.8 eV, 286.4 eV and 288.0 eV, corresponding to the C=C/

C—C, C=N/C—N and C=O/C—O bonds, respectively, which could further confirm the successful loading of COF TAPB-DMTA. The O 1 s spectra (Fig. S7B) could be deconvoluted into two characteristic features of O—H and O—C bonds, with peaks at 531.0 and 532.9 eV (Shi et al., 2022; Song et al., 2021). It verified the existence of –OH in TAPB-DMTA, alginate, PAA and C—O—C in TAPB-DMTA and sodium alginate. The Ca 2p spectra (Fig. S7C) normally displayed two characteristic peaks for Ca 2p3/2 and Ca 2p1/2 species centered at 347.5 eV and 351.1 eV, respectively, indicating the presence of Ca<sup>2+</sup> in the CACPs.

Contact angle measurements were utilized to investigate the hydrophilicity of CACPs and TAPB-DMTA. As can be seen in Fig. S8, the contact angles of CACPs and TAPB-DMTA were 42.79° and 83.94°, respectively, indicating that compounding with sodium alginate can significantly improve the hydrophilicity of TAPB-DMTA.

#### 3.4. Extraction optimization

CACPs were used as adsorbents for dSPE of five neonicotinoids in fruit and vegetables. To achieve the best efficiency, factors affecting the extraction of neonicotinoids were optimized, including pH, ionic strength, extraction time, the number of CACPs, eluent type, eluent volume, and elution time.

#### 3.4.1. Effect of pH and ionic strength

The pH of solution influences the extraction efficiency by changing the charge state of analytes. Hence, the pH was optimized from 3 to 9 (Fig. 3A), which was controlled by adding HCl or NaOH solution. The observed increase in peak areas of imidacloprid and acetamiprid with an increase in pH from 3 to 6 could be attributed to the ionization of the weakly basic pyridine ring under acidic conditions, which was not conducive to the adsorption (Liu et al., 2022). As the pH continued to increase from 6 to 9, the peak areas of both analytes decreased due to hydrolysis under alkaline conditions (Ghiasi et al., 2020). For clothianidin and thiamethoxam, the maximum peak area at pH 6 was owing to the fact that they degraded under acidic and basic conditions (Karmakar et al., 2009). Therefore, pH 6 was chosen as the experimental condition for subsequent dSPE.

It is well known that adding salt to the solution can reduce the solubility of analytes by salting out, which is positive for extraction. At the same time, the viscosity of solution rises with the increase in salt concentration, which is negative for extraction. Therefore, the ionic strength was optimized (Fig. 3B). The peak area of acetamiprid showed an increasing and then decreasing trend, and that of the other four neonicotinoid insecticides showed a decreasing trend with NaCl concentration increasing from 0 to 10% (w/v). For comprehensive



Fig. 3. The effect of (A) pH, (B) ionic strength, (C) extraction time, (D) eluent type, (E) eluent volume, (F) elution time, and (G) the number of CACPs on the extraction of five neonicotinoid insecticides and (H) cycles used of CACPs.

consideration, the concentration of NaCl was chosen as 0%.

#### 3.4.2. Effect of extraction time

The extraction time determines whether adsorption equilibrium is reached, thereby affecting the extraction efficiency. The optimization of extraction time ranged from 5 to 60 min (Fig. 3C). A notable increase in peak areas was seen when the extraction time was increased from 5 to 40 min, and then stabilized after 40 min, demonstrating that the extraction had reached equilibrium at this time. According to the obtained result, a 40 min extraction was chosen.

## 3.4.3. Effect of desorption conditions

Desorption conditions are the major factor influencing extraction efficiency. Firstly, it is crucial to select a suitable eluent, which is required to possess a favorable solubility for the analyte, while also having an appropriate elution capability to prevent adverse impacts on the reusability of the adsorbents (Niu et al., 2020). The elution performance of methanol, acetonitrile, 0.5% ammonia-methanol and 0.5% acetic acid-methanol was investigated (Fig. 3D). Acetonitrile showed better elution efficiency on acetamiprid and imidacloprid, but relatively poorer elution efficiency on dinotefuran, clothianidin and thiamethoxam. 0.5% ammonia-methanol and 0.5% acetic acid-methanol showed comparable elution efficiency with methanol. Methanol was finally selected as the subsequent eluent after comprehensive consideration.

Moreover, the eluent volume and elution time were also explored in the range of  $0.5 \sim 2$  mL and  $2.5 \sim 25$  min, respectively. As shown in Fig. 3E, the peak areas of five neonicotinoid insecticides exhibited a decreasing trend with increasing eluent volume, demonstrating that neonicotinoids had been completely eluted when using 0.5 mL methanol. Subsequently, the neonicotinoids were diluted as the eluent volume increased, resulting in the decrease in peak areas. In addition, the effects of eluting twice with 0.5 mL and 1 mL methanol were considered (the elution time remained consistent). The results showed that 0.5 mL methanol eluted once still exhibited the best efficiency. Therefore, 0.5 mL methanol was chosen for subsequent experiments. According to Fig. 3F, the peak areas of five neonicotinoid insecticides exhibited an increasing trend as the elution time progressed from 5 to 15 min. When it reached 15 min, the peak areas were virtually unchanged or slightly decreased, and the elution reached equilibrium. Therefore, the subsequent elution time was set to 15 min.

## 3.4.4. Effect of the number of CACPs

The number of CACPs directly affects the extraction efficiency, so it was investigated (Fig. 3G). The peak areas all increased significantly as the number of CACPs increased from 1 to 10, and increased slightly from 10 to 18, and the continued increase was not conducive to the subsequent elution. Therefore, the number of CACPs was chosen as 18.

#### 3.5. Method validation

## 3.5.1. Analytical evaluation parameters

Under the optimal conditions, the analytical evaluation parameters, including linearity, LOD, LOQ, precision and repeatability, were investigated to evaluate the applicability of the proposed CACPs-dSPE-HPLC method for detecting neonicotinoid insecticides (Table S1). The working curve (Fig. S9) with concentration in the range of 0.01  $\sim$  10  $\mu g~mL^{-1}$  showed a good linearity correlation (R $^2 \geq$  0.9963). The LODs ranged from 0.0028 to 0.0031 mg kg $^{-1}$  and LOQs were 0.01 mg kg $^{-1}$ . Additionally, the CACPs exhibited good repeatability with inter-day RSD  $\leq$  8.11% and inter-batch RSD  $\leq$  7.97%.

## 3.5.2. Durability of CACPs

The durability of adsorbents is an important criterion for evaluating their practical application potential, so the reusability of CACPs was also evaluated. After extraction, CACPs were soaked in 10 mL methanol and sonicated for 15 min twice to ensure complete removal of analytes, and then were employed for the next extraction cycle. According to Fig. 3H, after seven adsorption/desorption cycles, the extraction efficiency of CACPs could maintain above 90%, indicating that CACPs have good reusability. With further increase in the cycle times, the extraction efficiency decreased, which was probably attributed to the incomplete elution of neonicotinoids from CACPs, resulting in the reduction of adsorption sites. Therefore, the recycling times of the prepared CACPs was determined to be 7 times.

## 3.5.3. Matrix effect

The matrix-matched calibration curves and matrix effect values (% ME) of five neonicotinoid insecticides in fruit and vegetable samples were presented in Table S2 and Fig. 4A-E. Matrix effects can be positive or negative and can be classified into three categories: strong matrix effects (>50% and <-50%), moderate matrix effects ( $20 \sim 50\%$  and - $50 \sim -20\%$ ) and slight matrix effects ( $-20 \sim 20\%$ ) (Rutkowska et al., 2018). The results indicated that the %ME of peach, pear, lettuce, cucumber and tomato samples were - $33.66 \sim -6.49\%$ , - $21.94 \sim -8.49\%$ , - $23.68 \sim 13.00\%$ , - $8.42 \sim 9.65\%$  and - $18.40 \sim 14.61\%$ , respectively. It demonstrated that except for acetamiprid and clothianidin in peach, thiamethoxam in pear, and dinotefuran in lettuce, it showed slight matrix effects, confirming the feasibility of CACPs-dSPE-HPLC for determining neonicotinoids in fruit and vegetables.

#### 3.6. Real sample analysis

In order to assess the accuracy and applicability of the established method, it was used for the detection of five neonicotinoid insecticides in fruit and vegetables (peach, pear, lettuce, cucumber, tomato). As shown in Fig. S10 and Table 1, dinotefuran and clothianidin were detected in lettuce and cucumber samples, while these five neonicotinoid insecticides were not detected in peach, pear and tomato samples. Dinotefuran and clothianidin were detected at a level of 0.319 and 0.078 mg kg<sup>-1</sup> in cucumber, 0.105 mg kg<sup>-1</sup> and less than LOQ in lettuce, respectively, which were all lower than the MRLs specified in Chinese standard 2763–2021 (Table S3).

The prepared samples were spiked with the standard solution at three concentration levels for recovery determination: 0.2, 0.4, and 2 mg kg<sup>-1</sup> (n = 3). The recoveries exhibited a range of 73.6 ~ 116.2% with RSDs less than 9.9%, demonstrating that the developed CACPs-dSPE-HPLC method was appropriate for analyzing neonicotinoids in fruit and vegetables.

#### 3.7. Comparison with other methods

The developed method was evaluated in comparison to previous approaches for the determination of neonicotinoid insecticides (Table 2). The method had the advantages of a low consumption of organic reagents, wide linear range and easy operation, and the LODs were comparable with other methods, which could achieve the detection of trace neonicotinoids in fruit and vegetables. As adsorbents, CACPs were prepared under room temperature, which was simple, convenient, and eco-friendly, and could be reused more than seven times. Furthermore, CACPs allow convenient adsorbent separation by tweezers within 1 min. In contrast, conventional dSPE procedures using powdered materials (COF/MOF, etc.) as adsorbents usually require  $5 \sim 20$  min of centrifugation or filtration followed by removal of the supernatant to achieve adsorbent separation (Romero et al., 2022, Pezhhanfar et al., 2023).

#### 3.8. Possible adsorption mechanism

As described in 3.1, the predominant pore size distribution of CACP was 2.968 nm, while the molecular diameters of the five neonicotinoids ranged from 10.2 Å to 13.6 Å (Fig. S11), which indicated that the CACPs

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**Fig. 4.** Matrix effects on neonicotinoids (dinotefuran, clothianidin, imidacloprid, thiamethoxam, acetamiprid) in fruit and vegetable samples (A-peach, B-pear, C-lettuce, p-cucumber and E-tomato) and (F) typical chromatograms (270 nm) of fruit and vegetable samples spiked with neonicotinoids at 0.2 mg kg<sup>-1</sup>.

#### Table 1

The concentrations (mg kg	<sup>1</sup> ), recoveries (%	) and RSDs (%, $n = 3$	of five neonicotinoid insecticides in fru	it and vegetable samples.
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Sample	Spiked level (mg kg <sup>-1</sup> )	Recovery $\pm$ RSD (%) Dinotefuran	) Clothianidin	Imidacloprid	Thiamethoxam	Acetamiprid
Lettuce	0	$0.105\pm1.4$	< LOQ	ND	ND	ND
	0.2	$100.9\pm 6.6$	$100.0\pm5.4$	$90.5\pm9.8$	$103.3\pm3.0$	$106.6\pm2.5$
	0.4	$104.0\pm5.7$	$91.2 \pm 9.9$	$93.9\pm9.7$	$97.2\pm3.6$	$95.3\pm1.3$
	2	$99.3\pm7.9$	$90.9\pm5.6$	$90.8\pm5.1$	$95.7\pm3.6$	$91.9\pm5.1$
Cucumber	0	$0.319 \pm 2.5$	$0.078 \pm 0.2$	ND	ND	ND
	0.2	$92.1\pm5.4$	$99.5 \pm 6.4$	$102.6\pm2.6$	$97.0\pm7.6$	$100.8\pm5.4$
	0.4	$115.7\pm4.3$	$112.5\pm6.5$	$73.6 \pm 5.9$	$110.5\pm9.1$	$99.6\pm5.9$
	2	$92.8\pm3.1$	$102.6\pm2.5$	$102.6\pm2.0$	$98.5\pm3.0$	$98.0 \pm 7.2$
Tomato	0	ND	ND	ND	ND	ND
	0.2	$92.7\pm7.8$	$\textbf{88.0} \pm \textbf{8.0}$	$92.1\pm5.7$	$\textbf{76.6} \pm \textbf{9.1}$	$96.6 \pm 7.2$
	0.4	$84.1\pm8.1$	$98.5\pm2.5$	$99.3\pm6.4$	$105.4\pm7.5$	$99.1\pm4.3$
	2	$100.5\pm0.2$	$107.7\pm8.1$	$99.9\pm0.2$	$113.1\pm4.1$	$99.8\pm0.5$
Peach	0	ND	ND	ND	ND	ND
	0.2	$98.8\pm9.7$	$100.8\pm7.4$	$102.1\pm8.4$	$99.9 \pm 1.1$	$102.6\pm7.4$
	0.4	$88.2\pm9.9$	$\textbf{95.0} \pm \textbf{5.8}$	$94.3\pm8.7$	$116.2\pm8.5$	$95.9 \pm 6.1$
	2	$82.5\pm2.8$	$104.5\pm2.1$	$100.3\pm2.4$	$95.2\pm3.5$	$100.1\pm1.3$
Pear	0	ND	ND	ND	ND	ND
	0.2	$83.9\pm3.4$	$87.3 \pm 6.3$	$\textbf{86.4} \pm \textbf{2.2}$	$80.2\pm3.1$	$89.7 \pm 3.8$
	0.4	$101.5\pm0.8$	$100.2\pm0.3$	$104.6\pm1.3$	$107.1\pm1.5$	$106.0\pm1.9$
	2	$\textbf{88.9} \pm \textbf{7.7}$	$\textbf{87.3}\pm\textbf{1.5}$	$89.4 \pm 3.5$	$\textbf{88.4} \pm \textbf{8.7}$	$\textbf{88.8} \pm \textbf{1.5}$

ND: Not detected.

Table	2
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Comparison of the proposed method with other previously developed methods for the determination of neonicotinoid insecticides in food samples.

Determination method	Extraction method	Linear range (µg L <sup>-1</sup> )	LODs (µg kg <sup>-1</sup> )	RSD (%)	Organics volume (mL)	Recovery (%)	Reference
HPLC-DAD UPLC-MS/MS UPLC-MS/MS HPLC-MS/MS HPLC-DAD HPLC-DAD	QuEChERS <sup>a</sup> SPE <sup>b</sup> QuEChERS QuEChERS MSPE <sup>c</sup> dSPE <sup>d</sup>	$20 \sim 2500 \\ 10 \sim 500 \\ 8.1 \sim 100 \\ 10 \sim 6000 \\ 8 \sim 1000 \\ 10 \sim 10000$	$10 \sim 60 \\ 0.46 \sim 1.4 \\ 2.2 \sim 3.7 \\ 10 \\ 2.5 \sim 3.0 \\ 2.8 \sim 3.1$	<12 1.8 ~ 9.8 <20 11.87 $\leq$ 5.6 <8.11	5 15 10 20 0.2 0.5	$70.37 \sim 113.57$ $72.2 \sim 95.0$ $78.1 \sim 117.3$ $70 \sim 120$ $83 \sim 112$ $73.6 \sim 116.2$	(Mahdavi et al., 2020) (Zhang et al., 2018) (Zhao & Shi, 2022) (Rahman et al., 2015) (Jiang et al., 2022) This work

<sup>a</sup> quick, easy, cheap, effective, rugged, and safe; <sup>b</sup> solid-phase extraction; <sup>c</sup> magnetic solid-phase extraction; <sup>d</sup> dispersive solid-phase extraction.

could provide sufficiently large nanochannels for the movement and adsorption of the analytes. It demonstrated the existence of a pore-size matching effect between CACPs and neonicotinoids. Meanwhile, the strong adsorption interactions between CACPs and neonicotinoids may also be due to the  $\pi$ - $\pi$  interactions between their aromatic rings (Liu et al., 2022).

Fluorescence spectroscopy was conducted to explore the adsorption mechanism between TAPB-DMTA and neonicotinoids (Fig. S12). After adding imidacloprid, an increase in the fluorescence intensity at 530 nm and a slight blue shift were observed, and similar phenomena were observed for the other four neonicotinoid insecticides. This was ascribed to the multiple hydrogen-bonding interactions between TAPB-DMTA and neonicotinoids, including the interactions between the nitro group of dinotefuran, clothianidin, imidacloprid, thiamethoxam, the cyano group of acetamiprid and the free amino group of TAPB-DMTA, and the interactions between the imine group of TAPB-DMTA, which was favorable for the electronic transition (Wu et al., 2023).

The adsorption mechanism was further explored by comparing the XPS of CACP before and after neonicotinoid adsorption (Fig. S13). Characteristic elemental peaks of C 1 s, O 1 s, N 1 s, and Ca 2p were observed in the full XPS spectra of CACPs before and after neonicotinoid adsorption (Fig. S13A). The slight increase in the total C1 s and N1 s content after neonicotinoid adsorption compared to that before adsorption was attributed to the introduction of neonicotinoids (containing mainly C and N elements). From the high-resolution spectra of C 1 s (Fig. S13B) and N 1 s (Fig. S13D), it can be seen that the contents of C=C/C-C, C-N, and N-H increased significantly after the adsorption of neonicotinoids, which proved the successful adsorption of neonicotinoids. Analyzing in combination with the high-resolution spectra of O 1 s (Fig. S13C), a significant decrease in the peak intensity of C-O after adsorption of neonicotinoids accompanied by an increase in the binding energy was found. It demonstrated that -O-CH<sub>3</sub> (from TAPB-DMTA) in CACPs played an important role in the adsorption process, primarily by forming strong hydrogen bonds with -NH- of neonicotinoids (Zhang et al., 2023). Meanwhile, the peak intensity of -O-H increased significantly after adsorption, and the peak shifted slightly toward higher binding energy. It was attributed to the fact that sodium alginate in CACPs was abundant in -OH, which could form strong hydrogen bonds with -NH-, =N- and -C=N groups in neonicotinoid molecules, thus changing the binding energy and increasing the core orbital peak area (Wu et al., 2019). Before and after the adsorption of neonicotinoids, the positions and peak areas of the two peaks in the Ca 2p spectra (Fig. S13E) did not change significantly, indicating that the gel skeleton was stable during the adsorption process.

Furthermore, by comparing the extraction performance of CACPs for carbamate pesticides (fenobucarb, tsumacide, isoprocarb, carbaryl) and benzimidazole fungicides (carbendazim) (Table S4), it can be found that the extraction efficiencies were roughly negatively correlated with their log*Kow* values, suggesting that the polar interactions also play a key role in the adsorption of neonicotinoids by CACPs (Hassan et al., 2021).

Based on the BET, fluorescence spectroscopy, XPS and comparison experiment data, adsorption of the neonicotinoids on CACPs involved pore-size matching effect,  $\pi$ - $\pi$  interactions, hydrogen bonding and polar interactions (Fig. S14).

#### 4. Conclusion

In this study, COF TAPB-DMTA-based hydrogels CACPs were facilely prepared at room temperature, and were used for convenient dSPE of five neonicotinoid insecticides in fruit and vegetables. The hydrogen bonding,  $\pi$ - $\pi$  interactions, polar interactions and pore-size matching effects contributed to the good adsorption performance of the CACPs toward neonicotinoids. CACPs could be completely separated within 1 min without centrifugation, and maintained high extraction efficiencies (>90%) after seven adsorption/desorption cycles. The simple preparation procedures and the improved solid–liquid separation efficiency render the proposed composite strategy of adsorbents attractive for scale-up and practical application. Moreover, the effective adsorption of neonicotinoids makes this method promising for extension to the pretreatment of other polar organic pollutants.

#### CRediT authorship contribution statement

Ling-Zhi Liu: Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft. Rui Zhou: Data curation, Investigation. Yong-Li Li: Project administration, Resources. Yue-Hong Pang: Formal analysis, Funding acquisition, Investigation, Methodology, Validation. Xiao-Fang Shen: Conceptualization, Funding acquisition, Project administration, Resources, Writing – review & editing. Jun Liu: Funding acquisition, Project administration.

## **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.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2024.138357.

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