Analytical Methods

Facile synthesis and evaluation of three magnetic 1,3,5-triformylphloroglucinol based covalent organic polymers as adsorbents for high efficient extraction of phthalate esters from plastic packaged foods

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ABSTRACT

Three covalent organic polymers (COPs) were successfully fabricated by room-temperature solvent-free mechanochemical grinding method between 1,3,5-triformylphloroglucinol (TP) and *p*-phenyl enediamine (COP1), benzidine (COP2), 4, 4′′-diamino-p-terphenyl (COP3), and followed by coprecipitation on the surface of Fe_3O_4 nanoparticles to form three corresponding magnetic Tp-series COPs. The fabricated magnetic COPs were evaluated and then applied for the extraction of phthalate esters from food samples before gas chromatography-tandem spectrometry analysis. Magnetic COP2 exhibited the highest extraction efficiency, which can be attributed to its larger pore size, and its strong hydrophobic and π-π interactions with phthalate esters. The method possessed good linearity (10–1000 μg·kg^{-1}), high sensitivity (0.29–2.59 μg·kg^{-1} for LODs and 0.97–8.63 μg·kg^{-1} for LOQs), and satisfactory recoveries (70.2–108.1%) with relative standard deviations lower than 5.2%. This method has potentials for high efficient separation/preconcentration of hydrophobic phthalate esters from foods.

Introduction

Phthalate esters (PAEs) are commonly used as plasticizers in various plastic products to improve the flexibility, softness transparency, and durability properties (Kambiz, & Gordon, 2015; Chang et al., 2021). PAEs possess only physical bonding rather than covalent with plastic substrates, which enables their easy migration from the plastic packages to foods during the production and storage process (Peijnenburg, & Jaap, 2005; Rakkestad, et al., 2007) and eventually to humans (Guo, Qian, & Kannan, 2011; Salazar-Beltrán, et al., 2017). Studies have shown that long-term exposure to PAEs via food ingestion may cause adverse effects on human health, such as endocrine disorders, reproductive toxicity, teratogenesis, and carcinogenesis (Wang, et al., 2021; Fan, et al., 2017; Guo, et al., 2016; Yang, et al., 2015). In view of their potential hazards to human health, the use of certain PAEs such as di-*n*-butyl phthalate (DBP), benzyl butyl phthalate (BBP), di-2-ethylhexl

phthalate (DEHP), and di-*n*-octyl phthalate (DNOP) have been restricted in foods and plastic packages in China, the USA, and European Union (EU). In China, the maximum contamination amount of bis (2-ethylhexyl) phthalate (DEHP), di-*n*-butyl phthalate (DBP) in foods are set at 1.5, 0.3 mg kg^{-1}, respectively (Dobrzy, Tyrkiel, & Pachocki, 2011, Yang, et al., 2015). Therefore, measurement of PAEs residues in foods is of great importance for the security of human life and health.

Gas chromatography-tandem mass spectrometry (GC–MS/MS) has been the most widely used technique for identification and quantification of PAEs. However, due to their low levels in food samples and the complexity of the food sample matrix, an effective sample pretreatment is often required. Liquid-liquid extraction, dispersive liquid-liquid microextraction, accelerated solvent extraction, solid phase extraction, magnetic solid phase extraction (MSPE) have been employed for the analysis of PAEs (Pang, et al., 2020; Min, et al., 2020; Ma, et al., 2022; Yan, et al., 2017). Compared with other methods, MSPE is more simpler,

convenient and solvent-saving, which avoids tedious procedures such as centrifugation, filtration or conventional SPE column packing (Kumari, & Kaur, 2021; Iasa et al., 2020; Shan et al., 2021). Magnetic adsorbents can be easily and rapidly isolated from liquid solution through a magnet. Notably, facile synthesis of an efficient magnetic adsorbent is highly desirable for MSPE, and the extraction ability of magnetic adsorbents lies in selecting an appropriate adsorption material combined with magnetic Fe_3O_4 nanoparticles.

Covalent organic polymers (COPs) are a newly developing porous polymers with excellent characteristics, such as light density, great chemical stability, high surface area, adjustable pore structure, enabling them to be potential adsorbents. Among the series of COPs, 1,3,5-trifor-mylphloroglucinol (Tp) based COPs by covalent bonding with different amino monomers are emerging as a promising class of extraction materials and have showed great extraction performance for various target analytes via multiple interactions, such as hydrogen bonds, hydrophobic interaction, π-π interactions, steric effects and so on (Liu, et al., 2019; Wang, et al., 2018; Li, et al., 2018; He, et al., 2017). Besides, the Tp-based COPs is highly stable in water, even under basic or acidic conditions (Chandra, et al., 2013), showing great potential in sample pre-treatment application for foods. Given the good lipophilicity, abundant π-electrons and hydrogen-bonded receptor (carbonyl group) of PAEs, it is attractive and feasible to prepare Tp-series COPs with the proper amino monomers for the efficient extraction of PAEs from real samples. Recently, the room-temperature synthetic approaches under a simple and mild operational conditions have been developed and turned out to be a facile preparation method for COPs (Peng, et al., 2016).

Herein, three Tp-based COPs were fabricated in this work via the room-temperature solvent-free mechanochemical grinding approach, and the obtained COPs were magnetically functionalized on the surface of Fe_3O_4 via a coprecipitation approach. Subsequently, the extraction performance of the three magnetic Tp-series COPs (M−COPs) for PAEs, including M−COP1 (Fe_3O_4/COP-TpPDA), M−COP2 (Fe_3O_4/COP-TpBD) and M−COP3 (Fe_3O_4/COP-TpDT), were tentatively evaluated through the density functional theory (DFT) calculation and the adsorption experiments using other phenyl-containing compounds as model molecules. Among them, M−COP2 was revealed to be an promising adsorbent. Finally, the feasibility of employing M−COP2 for fast extracting PAEs from real food samples was investigated and optimized combined with GC–MS/MS. In addition, current research provide a simple route for the synthesis of magnetic Tp-based COPs, thus probably promoting the simultaneous determination of multiple PAEs in food samples.

Materials and methods

2.1. Materials and reagents

Tp, *p*-phenylenediamine (PDA), benzidine (BD), 4,4″-diamino-pter-phenyl (DT), ferrous chloride ($FeCl_2 \cdot 4H_2O$) and ferric chloride ($FeCl_3 \cdot 6H_2O$) were provided by Macklin (Shanghai, China). HPLC-grade methanol, acetonitrile and acetone were supplied by Aladdin Reagents Corporation (Shanghai, China). Standard PAEs mixture, including benzyl butyl phthalate (BBP), di-*n*-butyl phthalate (DBP), di-*n*-octyl phthalate (DNOP), bis (2-ethylhexyl) phthalate (DEHP), diisoheptyl phthalate (DIHP), diisodecyl phthalate (DIDP), and dipentyl phthalate (DPP) were obtained from O2si Smart Solutions (Charleston, USA). The stock solution of the PAEs with the concentration of 100 mg mL^{-1} was prepared in methanol and stored at −20 °C. A series of working solutions of PAEs were prepared by appropriate dilution of the stock solution before use.

2.2. Instrumentation

Morphological structure was observed by scanning electron microscopy (SEM) (SUPPATM 55, Zeiss, Germany). Fourier transform infrared

spectroscopy (FT-IR) spectrum was recorded on an FT-IR spectrometer (Nicolet 710 IR, California, USA). X-ray diffraction (XRD) data was conducted on a Siemens D500 diffractometer (Karlsruhe, Germany). The Magnetic hysteresis loops were studied on a PPMS 9 vibrating sample magnetometer (VSM) (Quantum Design, USA). The GC–MS/MS analysis was carried out on a Thermo Scientific TRACE 1310 gas chromatograph equipped with a Thermo Scientific TSQ 9000 triple quadrupole mass spectrometer with an electron ionization (EI) source, and a TriPlus RSH auto sampler and a split/splitless injector (Thermo Fisher Scientific, Waltham, USA). The operation, data aquisition and data analysis were performed on Chromeleon Software Version 7.2.8. The GC–MS/MS parameters are detailed in Supplementary Material. The molecular structure, GC retention times, optimized mass spectrum parameters and log *P* of seven PAEs are showed in Table S1.

2.3. Sample collection and preparation

Food samples either in plastic packing or plastic containers were purchased from local markets (Shijiazhuang, China), including apple, cucumber, and drinking water. A food processor was used to homogenize the samples thoroughly. The homogenized food samples were stored at −20°C. The samples were allowed to thaw at room temperature before use. All glassware that are inevitably used need to be washed by *n*-hexane and dried at 120 °C about 4 h before use for the sake of prevention of PAEs pollution. To eliminate or decrease the possibility of PAEs pollution and migration, all plastic products and organic solvents used in the experiment should be previously detected by GC–MS/MS (Luo, Yu, Yuan, & Feng, 2012; Pang, Yue, Huang, Yang, & Shen, 2020).

For each analysis, 0.5 g of sample was dissolved in 10 mL acetonitrile in a 50 mL centrifuge tube and then vortexed for 1 min. The mixtures were ultrasonically extracted for 30 min. After centrifuging for 5 min at 8000 rpm, the supernatant was dried under an N_2 atmosphere. Finally, the extracts were redissolved in 0.5 mL methanol and diluted with deionized water for the following MSPE-GC–MS/MS procedure. The drinking water was submitted directly to the MSPE-GC–MS/MS procedure, without any preparation steps.

2.4. Synthesis of M−COPs

Synthesis of COPs. COP1 (TpPDA), COP2 (TpBD), COP3 (TpDT) were synthesized using Schiff base aldehyde-amine condensation reactions via solvent-free mechanochemical grinding method under the room-temperature according to the reported method (Biswal, et al., 2013) with some modification. Tp (0.30 mmol) and either PDA (for TpPDA), BD (for TpBD), or DT (for TpDT) (0.45 mmol) were grounded with a pestle in a mortar at room temperature for 40 min. After completion of grinding, the dark-red powdered material was obtained, indicating the complete formation of COPs. Finally, the prepared COPs were dried under vacuum.

Synthesis of M−COPs. Magnetization of COP1, COP2 and COP3 on the surface Fe_3O_4 was synthesized by a coprecipitation method (Pan, et al, 2020). 0.5 g $FeSO_4 \cdot 7H_2O$ and 0.8 g $FeCl_3 \cdot 6H_2O$ were dispersed a three-neck round-bottom flask with pure water (200 mL). 70 mg of each synthesized COP was added to the above aqueous suspension. The suspension was continued to be thoroughly stirred at 80 °C, and then was adjusted to pH 10 by dropwise addition of 30% ammonia solution to the flask. After suspension turned dark brown, the reaction continued to stir at 80 °C for 30 min. The obtained M−COP1, M−COP2 and M−COP3 were washed with pure water and ethanol and then dried at 45 ℃ under vacuum. The schematic synthesis of the three COPs and M−COPs was shown in Fig. 1.

2.5. Magnetic solid-phase extraction (MSPE) procedure

Briefly, 10 mg of each magnetic adsorbent was added to 10 mL of sample extracts. The extraction process was carried out by vortex for 0.5
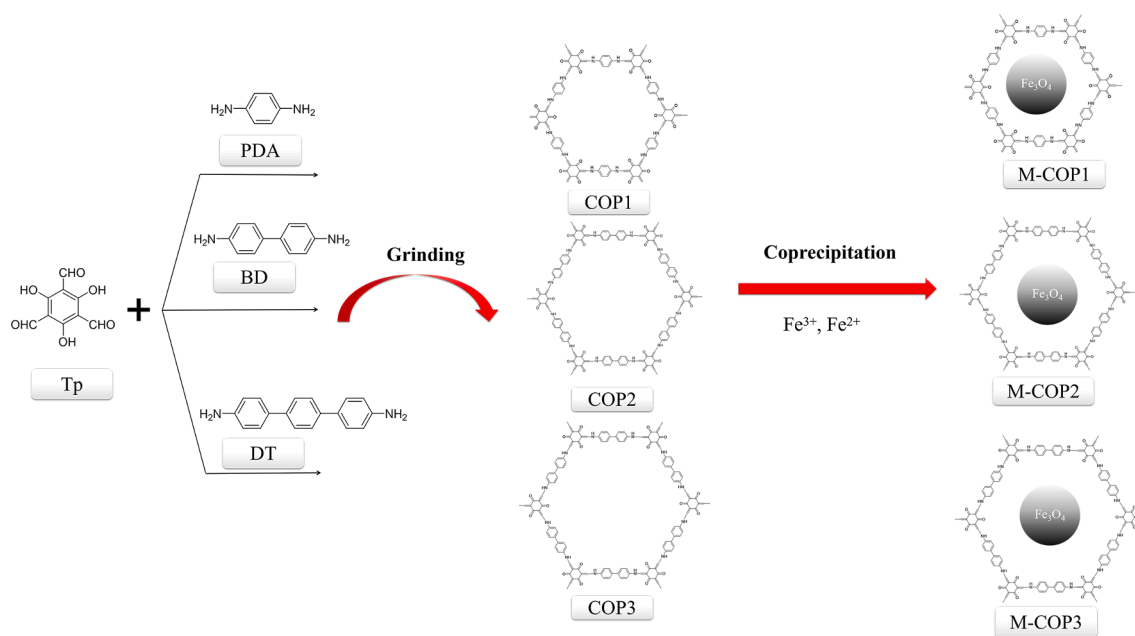
Fig. 1. The schematic synthesis of the COPs and M−COPs.

min, Then, the magnetic adsorbent were separated and collected using an external magnet. Afterwards, 0.5 mL of acetonitrile was added to elute the analytes from the magnetic adsorbents by vortex for 1 min. The collected eluent was filtered with a 0.22 μm membrane before GC–MS/MS analysis.
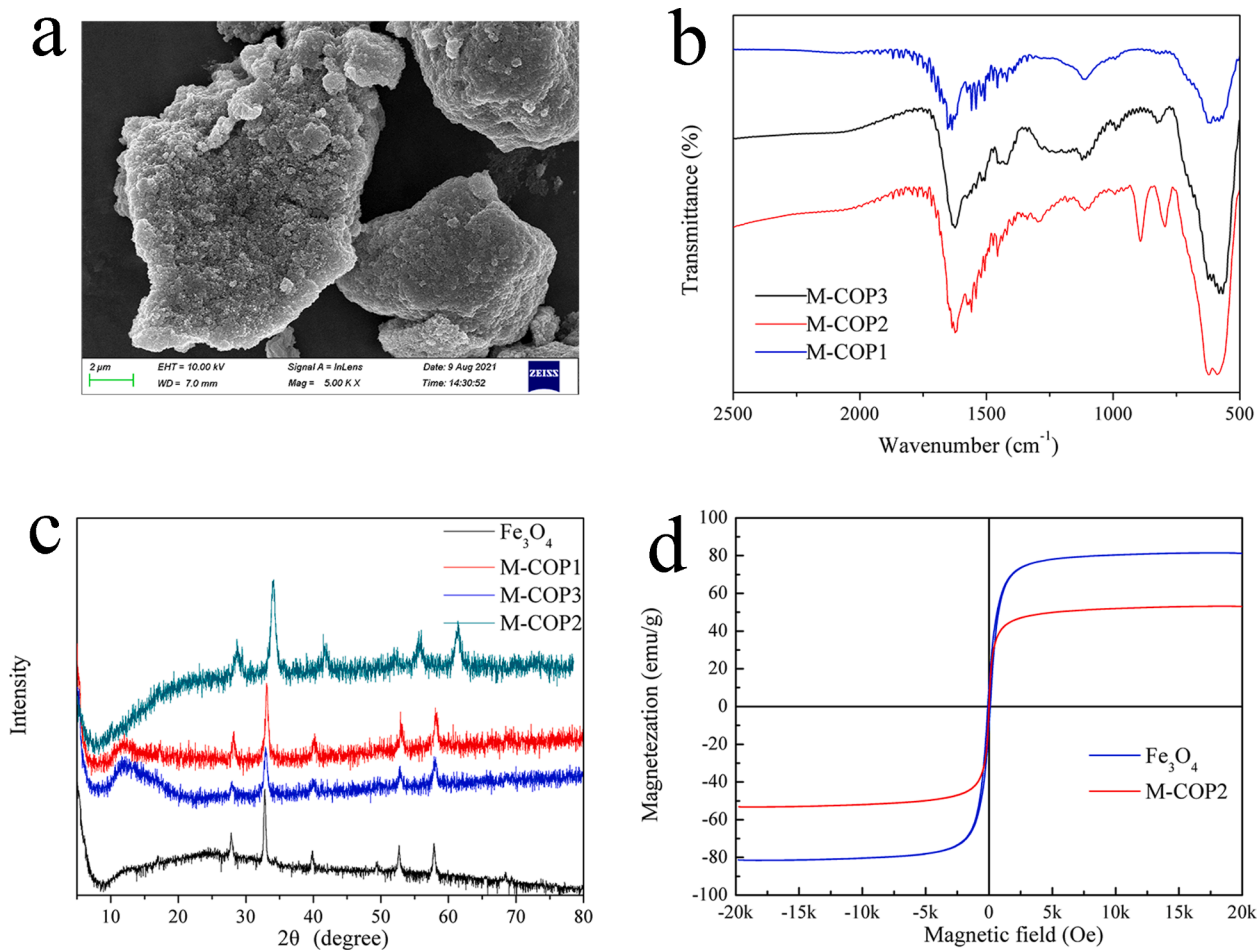

Fig. 2. SEM images (a), FT-IR spectra (b) and XRD patterns (c) and Magnetization curves (d).

Results and discussion

3.1. Characterization of M−COPs

The representative morphology of M−COP2 was characterized by scanning electron microscopy (SEM). From Fig. 2a, the prepared M−COP2 showed rough surface, indicating the embedment of Fe_3O_4 nanoparticles in each sheet matrix of COPs. The large specific surface area is advantageous for the absorption of the target analytes. To ensure the successful synthesis of the three M−COPs, the chemical composition and structure information of the synthesized M−COPs were further analyzed by FT-IR spectroscopy (Fig. 2b). The peak at 588 cm^{-1} was attributed to the stretching vibration of Fe-O-Fe of Fe_3O_4, indicating that three M−COPs have been successfully magnetized. The adsorption at 1624 cm^{-1} was ascribed to C═N vibration, and adsorption at 1252 cm^{-1} belonged to C─N ring stretching, indicating the new bond formation and subsequently the construction of the Tp-series COPs. Wide-angle XRD of three M−COPs was displayed in Fig. 2c. The typical diffraction peaks at 31.0, 35.3, 42.7, 53.4, 57.9 and 63.2° correspond to the structure of Fe_3O_4 crystals, which indicate the magnetization of three Tp-series COPs and well crystallized. The saturation magnetization values of Fe_3O_4 and the representative prepared M−COP2 are 81.0 and 51.7, respectively (Fig. 2d). Such a high saturation magnetization allows the prepared magnetic adsorbents to be fast response to external magnetic fields.

3.2. Possible adsorption mechanism

Bonding with different amino monomers is tuning the pore size of TP-based COPs, and the pore size is considered an effective criterion for adsorption properties. The inflence of the pore size on the adsorption properties was investigated using a DFT calculation by clarifying the tested molecule adsorption on each of three Tp-series COPs. The DIDP molecule with the largest molecule size (18.186 Å) of PAEs was employed as tested molecule to explore the adsorption characteristics. Detailed information of DFT calculation were described in Supplementary material. The optimized geometrical structures were obtained by a DFT calculation method and the pore sizes were about 22.66, 30.12 and 37.62 Å for the COP1, COP2 and COP3, respectively (Fig. 3a). The DIDP molecule tended to be adsorbed on the edge of the COP1, COP2 and COP3 pores, especially for COP3 with larger pore diameter. The results indicated that the pore sizes of three prepared Tp-based COPs would enable the DIDP molecule to diffuse into the pore without obvious steric effects. In comparison with COP1, the larger pore size of COP3 and COP2 will increase the affinity of the pore structure for the DIDP molecule. The calculation of the adsorption energy ($E_{sorption}$) values of DIDP on COP1, COP2, and COP3 were −1.17, −1.20 and −1.35 eV, respectively, due to the higher the absolute amount of adsorption energy, the better the adsorption process. Moreover, the negative energy resulting from the DIDP molecule and the COPs interactions in this work has shown the stable adsorption of the DIDP molecule by COPs. Even so, the relatively higher absolute amount of adsorption energy will decrease the tendency of DIDP molecules to escape from the adsorbents and thus hinder its desorption process, it is suggested to select the COP2/M−COP2 for extracting PAEs in the experiment.

The affinity, usually related to multiple interactions involving hydrophobic interactions, hydrogen bonding interactions, and $\pi-\pi$ interactions have been further investigated to evaluate the adsorption performance of three M−COPs through the adsorption experiments on other target molecules, in which a series of benzene substituents were employed as model molecules. Detailed information about the adsorption experiments were described in Supplementary material. The $\pi-\pi$ interactions can occur between the abundant aromatic groups throughout PAEs and the networks of COPs/M−COPs. The strong lipophilicity is the characteristics of COPs/M−COPs with a hydrophobic skeleton, which can contribute to the hydrophobic interaction with

seven target PAEs. Octanol-water partition coefficients (log P) of the target PAEs were were calculated by ChemBioOffice 2014 ranging from 4.16 to 8.99. The hydrogen bonding can be formed with the H-bond acceptors and H-bond donors on the surface of M−COPs (nitrogen-containing groups or carboxyl group) and PAEs (carboxyl group). As shown in Fig. 3b, the extraction efficiencies of naphthalene (NAP), phenanthrene, benzo[*a*]anthracene, benzo[*a*]pyrene and dibenzo[*a, h*] anthracene increased with the increasing number of conjugated double bonds and condensed rings for three M−COPs. log P of aniline, nitrobenzene, 2-chlorophenol, naphthalene, acenaphthylene, acenaphthene, phenanthrene, benzo[*a*]anthracene, benzo[*a*]pyrene and dibenzo[*a, h*] anthracene were calculated by ChemBioOffice 2014 to be 1.23, 1.83, 2.20, 3.03, 3.35, 3.51 4.03, 5.03, 5.34 and 6.02, respectively. As shown in Fig. 3b, the extraction efficiencies of naphthalene, acenaphthylene, acenaphthene, phenanthrene, benzo[*a*]anthracene, benzo[*a*]pyrene and dibenzo[*a, h*]anthracene increased with the larger log P values. The results revealed that M−COPs can readily adsorb high hydrophobic organic compounds than organic compounds with low hydrophobicity, confirming that hydrophobic interaction plays an important role in the adsorption. Note that acenaphthylene possessed one more double bond than acenaphthene, but a lower log P value which lead to lower hydrophobic interaction and thus lower extraction efficiency. And the extraction efficiencies of the three prepared M−COPs for the same target compounds, either with the larger values of log P or increasing number of conjugated double bonds were nearly as following order: M−COP2≈M−COP3 > M−COP1. Compared to 2-chlorophenol and nitrobenzene, aniline with lower log P value and lower lipophilicity but higher recoveries, which revealed that the hydrogen bonding formed with the amino-group in the aniline and the carboxyl group on the surface of M−COPs improved the extraction efficiency, indicating hydrogen bonding interactions also plays an critical role in the adsorption. And M−COPs showed the extraction efficiencies orders for 2-chlorophenol and nitrobenzene, aniline as follows: M−COP2 > M−COP1 ≈ M−COP3.

Considering the above-mentioned, the M−COP2 will be a good choice for the extraction of the PAEs and further confirmed by the MSPE experiment. The possible adsorption mechanism between PAEs and M−COP2 was demonstrated in Fig. 3c.

3.3. Optimization of MSPE conditions

3.3.1. The choice and amount of adsorbent

The selection of proper adsorbent plays a significant role in extraction performance. In this study, the three M−COPs (10 mg for each) for MSPE of PAEs were evaluated in terms of their extraction efficiencies. As displayed in Fig. 4a, the two composite adsorbents of M−COP2 and M−COP1 had higher extraction with the recoveries of 71.4–104.6% and 70.6–101.3%, respectively. Meanwhile, no significant difference in recoveries (70.48–96.07%) was observed when 5 mg M−COP2 and 5 mg M−COP1 were combined to use as an adsorbent in the experiment. After the comprehensive evaluation, M−COP2 was selected as the adsorbent for further use in this study. After that, amounts (5, 10, 12, 15 and 20 mg) of M−COP2 were also optimized. The results in Fig. 4b showed that recoveries increased as M−COP2 increased from 5 mg to 10 mg, and recoveries stayed almost constant with increasing the adsorbent amount from 10 mg to 20 mg, indicating that 10 mg was sufficient for the subsequent MSPE procedure.

3.3.2. The pH value of sample solution

The sample solution pH could affect the existence forms of PAEs and the surface property of M−COP2, then impact the extraction efficiencies. In this work, the influence of pH values (5, 6, 7, 8 and 9) on the extraction efficiency were studied. From Fig. 4c, there were slight fluctuations but no obvious difference in extraction efficiency as pH change from 5.0 to 7.0. As pH increased from 7.0 to 9.0, the recoveries showed obvious decrease. Therefore, sample solution pH was set to
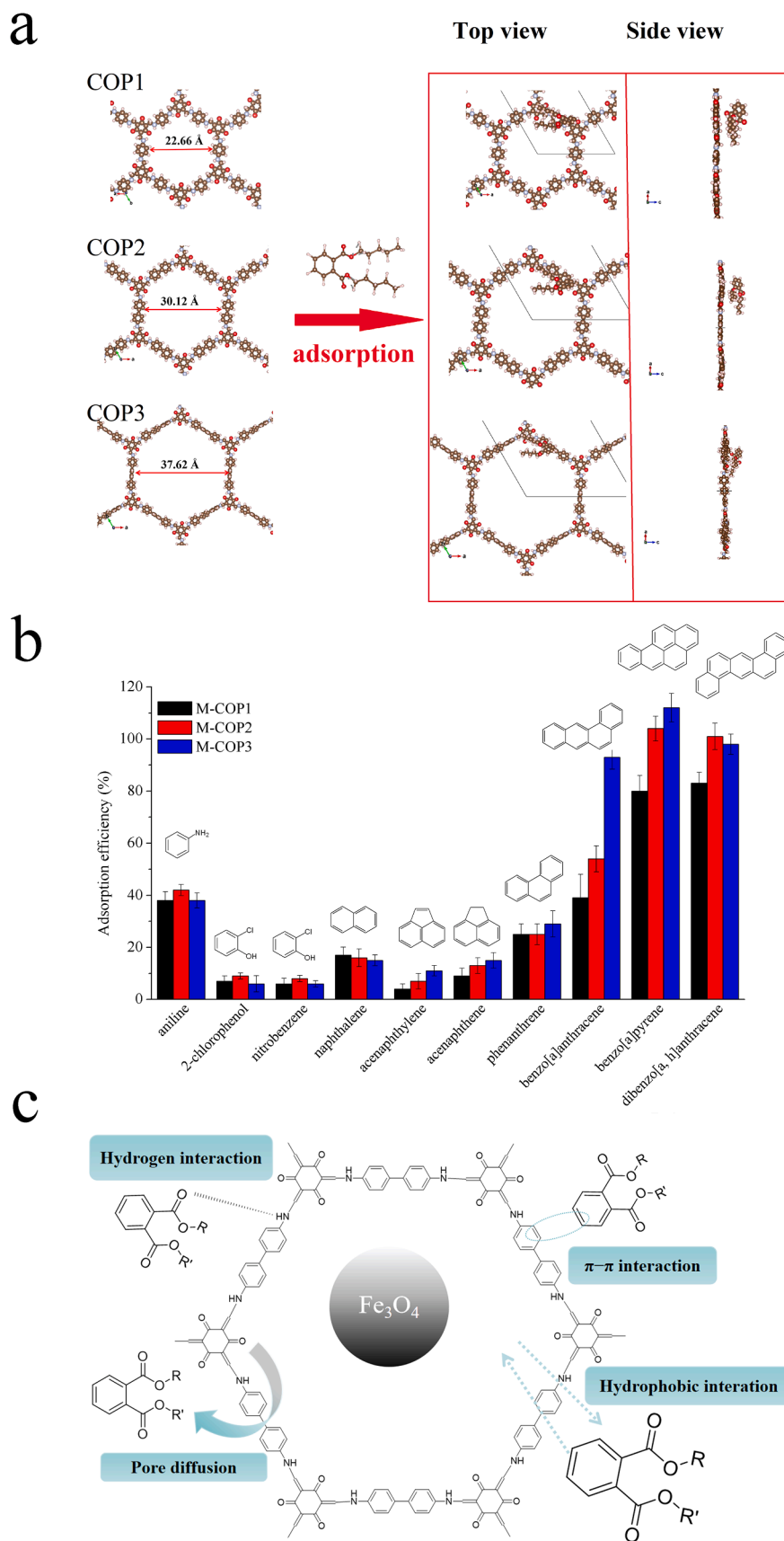
Fig. 3. Optimized geometrical structures for the adsorption of DIDP on COP1, COP2, and COP3 obtained via DFT (a), adsorption efficiencies of benzene substituents (b), and possible adsorption mechanism of the PAEs by M−COP2 (c).
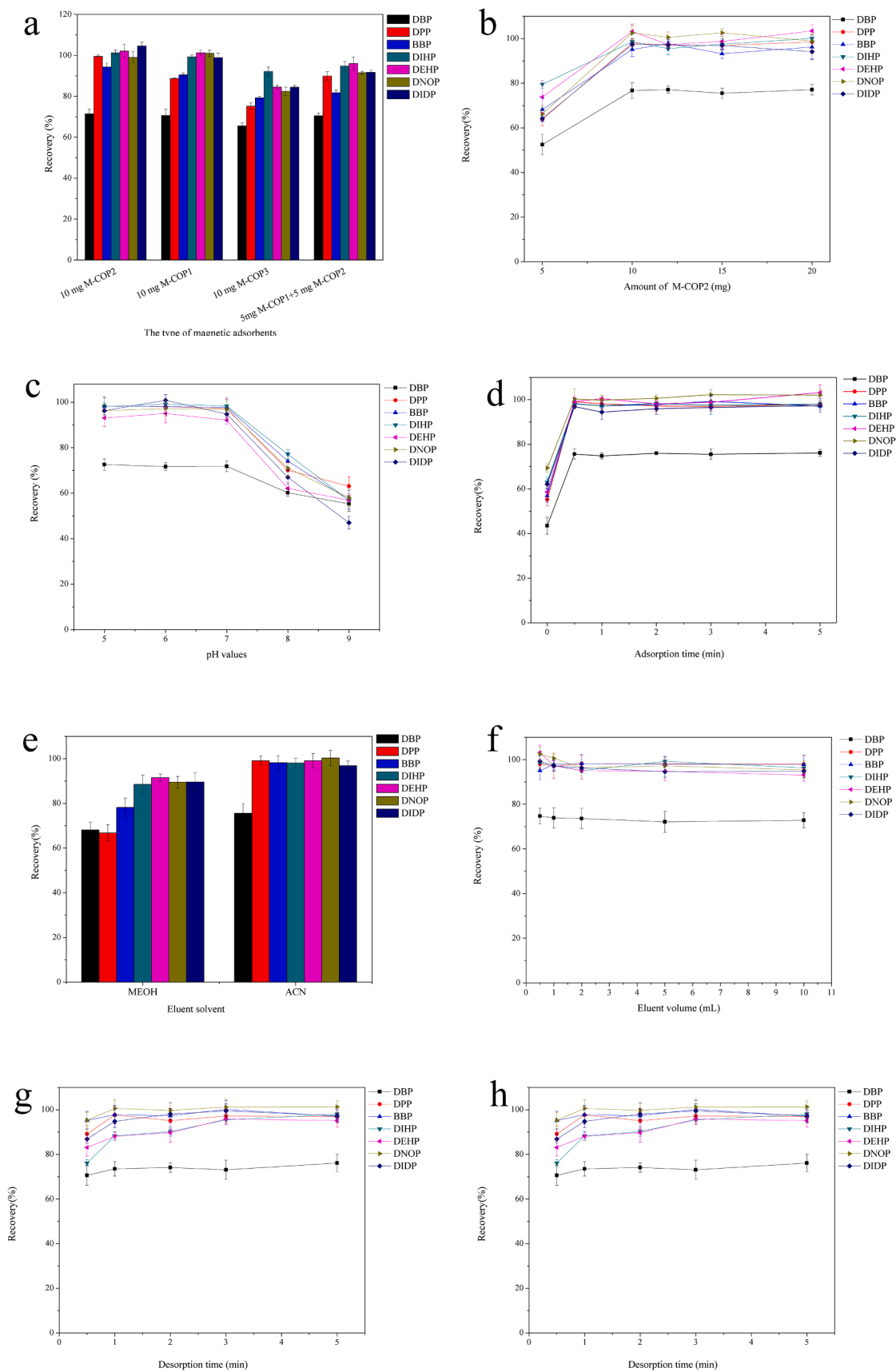
Fig. 4. Effects of the choice of magnetic adsorbents (a), the amount of M−COP2 (b), pH of sample solution (c), extraction time (d), eluent solvent (e) and volume (f), desorption time (g) and the reproducibility of M−COP2 (h) on the PAEs extraction efficiency.

5.0–7.0.

3.3.3. Extraction time

The vortex agitation can increase the contact area between the magnetic adsorbent and analytes, then accelerate the adsorption of the analytes onto the adsorbent. As shown in Fig. 4b, the effects of different vortex times (0.5–5 min) were investigated on the extraction efficiencies and 0 min represents the comparison test using static extraction time of 30 min. Without assistant of vortex agitation, the recoveries were in the range of 43.5%-69.3%. While the vortex treatment could obviously enhance the recoveries of PAEs and there was no significant difference between 0.5 min and 1 min, which both resulted in recoveries ranging from 74.8% to 100.4%. But further prolonging the vortex time had no significant change. Hence, 0.5 min was selected as the optimal adsorption time.

3.3.4. The type and volume of elution solvent

To investigate the influence of elution solvent on the extraction efficiency, the commonly used methanol (MeOH) and acetonitrile (ACN) were studied for the desorption of the analytes from the magnetic adsorbents. As shown in Fig. 4e, ACN performs better than methanol. Subsequently, the eluent volume of ACN was studied in the range of 0.5–10 mL. According to Fig. 4f, the optimal extraction efficiency is obtained when using 0.5 mL of ACN, and further increasing the eluent volume had no obvious change but reduced the enrichment effect. Thus, 0.5 mL ACN was selected for the further experiments.

3.3.5. Desorption time

Desorption time had a great impact on desorption efficiency. To facilitate the transfer of analytes into the eluent solvent, another vortex step is needed. Different vortex time for desorption (0.5–5 min) was investigated. Fig. 4g showed 1 min was enough to achieve high elution efficiency, there was no significant increasing of the elution efficiency as eluting time further extended to 5 min. As a result, 1 min was adopted as desorption time for the subsequent experiment.

3.3.6. Reusability of the magnetic adsorbent

The reproducibility of M−COP2 was investigated by conducting five consecutive MSPE cycles under optimized conditions in terms of changes in the percentage of recovery. M−COP2 was rinsed with ACN before each cycle. As seen in Fig. 4h there is no obvious decreases of recoveries after five cycles, indicating that M−COP2 adsorbent had good reusability.

3.4. Method validation and comparison

The typical chromatograms of mixture standard solution of each PAE at 500 μg kg^{-1} and the blank drinking water were showed in Fig. S1, and the blank drinking water spiked at 500 μg kg^{-1} after MSPE using the three M−COPs were showed in Fig. S2. Compared with chromatograms of PAEs extracted by M−COP1 and M−COP3, it was proved that M−COP2 could be used as an effective adsorbent. The analytical performance of the established M−COP2 based MSPE-GC–MS/MS method was validated in terms of linearity, sensitivity (limit of detection (LOD) and quantification (LOQ)), and precision. LODs, refered to signal-to-noise ratios (S/N) at 3, were 0.43–2.32 μg kg^{-1} in drinking water, 0.29–2.59 μg kg^{-1} in apples, and 0.46–2.01 μg kg^{-1} in cucumbers (Table 1). LOQs, refered to S/N at 10, were 1.43–7.73 μg kg^{-1} in drinking water, 0.97–8.63 μg kg^{-1} in apples, and 1.53–6.70 μg kg^{-1} in cucumbers (Table 1). The matrix-matched calibration curves were established by analysis of spiked food samples at different concentration levels. Good linearity were obtained in the range of 10–1000 μg kg^{-1} with a high correlation coefficient (R^2 > 0.9953) (Table 1). The intra-day and inter-day RSD values were lower than 4.1% (n = 3) and 5.6% (n = 3) in food matrices, respectively (Table 1).

Additionally, the analytical performance of the M−COP2 based

Table 1
Analytical performances of the proposed method in drinking water, apple and cucumber samples.

Analytes	Samples	R^2	LODs (μg kg^{-1})	LOQs (μg kg^{-1})	Intra-day RSD (%)	Inter-day RSD (%)
DBP	Drinking water	0.9998	0.43	1.43	3.1	2.9
	Apple	0.9976	0.39	1.30	1.9	3.6
	Cucumber	0.9989	0.78	2.60	4.1	4.2
DPP	Drinking water	0.9984	0.65	2.17	2.1	3.1
	Apple	0.9959	0.29	0.97	3.2	3.1
	Cucumber	0.9967	0.46	1.53	2.8	2.9
BBP	Drinking water	0.9992	1.63	5.43	3.9	4.2
	Apple	0.9987	1.51	5.03	2.5	3.1
	Cucumber	0.9990	1.36	4.53	3.0	3.8
DIHP	Drinking water	0.9988	0.61	2.03	1.8	1.2
	Apple	0.9986	0.72	2.40	1.9	2.9
	Cucumber	0.9975	0.68	2.27	2.6	3.1
DEHP	Drinking water	0.9968	1.03	3.43	2.3	2.3
	Apple	0.9980	0.99	3.30	4.1	4.1
	Cucumber	0.9982	0.87	2.90	2.9	4.2
DNOP	Drinking water	0.9953	2.12	7.07	0.7	1.9
	Apple	0.9965	2.51	8.37	2.3	3.9
	Cucumber	0.9973	2.01	6.70	4.1	5.6
DIDP	Drinking water	0.9990	2.32	7.73	1.5	2.3
	Apple	0.9991	2.59	8.63	2.5	3.6
	Cucumber	0.9993	1.90	6.33	1.7	3.2

MSPE method was compared with other reported methods for the analysis of PAEs (Table 2). Compared with other reported MSPE methods, the current method presented a fast and efficient MSPE procedure using only a small amount of magnetic adsorbent. Using 10 mg of M−COP2, the MSPE process of adsorption and desorption only took 0.5 min and and 1 min, respectively, which is much less than other reported method. Additionally, the M−COP2 based MSPE-GC–MS/MS method exhibited satisfactory LODs, accuracy and precision. LODs (0.29–2.59 μg kg^{-1}) of the developed method can meet the requirements for determination of PAEs in foods. Except for the recoveries of DBP (70.2–77.0%), recoveries (89.6–108.1%) of the proposed methods are higher than or equal to other methods. And the RSDs (<5.2%) in this work are comparable to or even better in comparison to other methods. Furthermore, a feasible and simple synthesis procedure renders M−COP2 attractive candidates for MSPE application. The proposed method turned out to be fast, sensitive and reliable and has exhibited great potential for the determination of PAEs in real samples.

3.5. Application to real samples

The applicability and accuracy of the proposed M−COP2 based MSPE method were confirmed by analyzing target PAEs in three common plastic packaged food samples (apple, cucumber and drinking water) (Table S2). The results of spiked recovery experiments (10, 100, and 500 μg kg^{-1}) have showed that the recoveries of PAEs in apple, cucumber and drinking water samples were 70.2–106.2%, 70.0–102.1% and 73.2–108.1%, respectively. The RSDs for apple, cucumber and drinking water samples were found to be 1.3–4.6%, 1.2–3.9% and 1.1–3.8%, respectively. The results confirmed that the proposed method is reliable, accurate and sensitive for analyzing trace PAEs in real food samples.

Conclusion

In summary, a series of magnetic Tp-based COPs were successfully

Table 2
Comparison of the proposed method with other MSPE methods for determination of PAEs using magnetic material.

Samples	Detections	Magnetic adsorbents	The ratio of material to sample	Adsorption time (min)	Desorption time (min)	LODs	Recoveries (%)	RSDs (%)	Ref.
Plastic pottled beverages	GC-FID	Magnetic dummy molecularly imprinted microspheres (MAG-MIM)	100 mg/10 mL	10	5	0.53–1.2 µg L^{-1}	89.5–101.3	<6.9	(Qiao, Wang, Yan, & Yang, 2014)
Environmental water samples	HPLC-DAD	Fe$_3$O$_4$@ZIF-8	20 mg/20 mL	8	8	0.08–0.24 µg L^{-1}	85.6–103.6	<5.5	(Liu, et al., 2015)
Edible vegetable oils	HPLC-UV	Fe$_3$O$_4$@COF(TbBD)	30 mg/30 mL	20	10	0.55–0.9 µg kg^{-1}	80.2–102.9	<7.9	(Zhao, Zhu, Liu, Liu, & Li, 2021)
Plastic bottled pear juice and pineapple juice	HPLC-UV	Magnetic HAzo	15 mg/50 mL	20	0.75	0.08–0.50 µg L^{-1}	78.0–115.0	<7.8	(Wu, et al., 2021)
Environmental water samples	GC–MS	Fe$_3$O$_4$/ZIF-67	20 mg/50 mL	15	–	0.005–0.035 µg L^{-1}	81.2–107.2	<10.5	(Zhang, Liu, Cao, Yin, & Zhang, 2020)
Human plasma samples	GC–MS	Fe$_3$O$_4$@PDA@mSiO2@ZIF-8	5 mg/10 mL	5	5	50–80 µg L^{-1}	90–105	<4.9	(Wang, Liu, & Yan, 2021)
Apple, cucumber, drinking water	GC–MS	Fe$_3$O$_4$/COP-TpBD	10 mg/10 mL	0.5	1	0.29–2.59 µg kg^{-1}	70.2–108.1	<5.2	This work

fabricated, evaluated and applied as adsorbents for MSPE of PAEs from food samples. Compared with other proposed MSPE methods, current method consumed less magnetic adsorbent and presented time-saving adsorption/desorption process. Under the optimal MSPE conditions, the method possessed ideal linearity, low LOQs, satisfactory accuracy and precision and good practicability. Furthermore, the adsorption mechanism were systematically revealed via DFT calculations, adsorption experiments for phenyl compounds. As results, the three prepared M−COPs composites exhibited great extraction potential for PAEs, especially using M−COP2 as adsorbent, where the larger pore size, strong hydrophobic and π-π stacking interactions were the synergetic interaction forces between the magnetic adsorbent and the target analytes. Predictably, the novel series of magnetic Tp-based COP composites may become a class of efficient adsorbents for monitoring many other pollutants in complex food samples, particularly for pollutants with relatively higher log *P* or large numbers of fused rings or conjugated double bonds, which will promote the development of food safety. Hence, further work is still needed to explore their selective adsorption and applications in complex samples.

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.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2022.100346.

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