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# Magnetic solid-phase extraction using polydopamine-coated magnetic multiwalled carbon nanotube composites coupled with high performance liquid chromatography for the determination of chlorophenols†

Wenhui Lu, [ID] *[a] Shanchao Fu,[a] Xiaoze Sun,[a] Jie Liu,[b] Deyi Zhu, [ID] [a] Jinhua Li[b] and Lingxin Chen [ID] *[b,c]

Polydopamine (PDA)-coated magnetic multiwalled carbon nanotube (M-MWCNT) composites were synthesized in two facile preparation steps, and were used as adsorbents for magnetic solid-phase extraction (MSPE) coupled with high-performance liquid chromatography (HPLC) for simultaneous extraction, enrichment and determination of five kinds of typical chlorophenols (CPs) in water samples. The as-prepared magnetic composites showed excellent magnetic properties and high thermal stability. Various main parameters influencing the extraction efficiency of MSPE were systematically investigated. Under the optimized MSPE–HPLC conditions, a high enrichment factor (EF) was obtained in the range of 85–112 for 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,6-dichlorophenol (2,6-DCP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP). Good linearity was obtained in the range of 2.0–200 μg L$^{-1}$ for 2-CP and 4-CP and 1.0–200 μg L$^{-1}$ for 2,6-DCP, 2,4-DCP and 2,4,6-TCP, with a correlation coefficient ($R^2$) higher than 0.9964. The limits of detection (LODs) and the limits of quantification (LOQs) were in the range of 0.10–0.31 μg L$^{-1}$ and 0.35–1.03 μg L$^{-1}$, respectively. The intraday and interday precisions evaluated using relative standard deviation (RSD) values were in the range of 1.05–2.25% and 1.88–2.83%, respectively. The validated MSPE–HPLC method was also successfully applied to analyze five kinds of CPs in tap water, lake water, river water and seawater samples, and satisfactory recoveries were obtained in the range of 76.87–106.5% with RSDs of 1.64–6.78%.

## Introduction

Chlorophenols (CPs) as a kind of excellent broad-spectrum bactericide have long been used in the pharmaceutical, textile, papermaking and leather industries. Based on their strong toxicity, pungent odor and carcinogenic properties, some of them have been listed as priority pollutants by the U.S. Environmental Protection Agency (EPA) and prohibited from usage, such as 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-

DCP), 2,4,6-trichlorophenol (2,4,6-TCP) and pentachlorophenol (PCP). As reported, CPs have been detected in water sources, wastewater, soil, sediments, aquatic organisms and human urine at the ng L$^{-1}$–mg L$^{-1}$ concentration level.[1–3] Therefore, sensitive, accurate and effective methods are necessary for the analysis of low levels of CPs in complicated matrices.

Until now, gas chromatography (GC) with electron-capture detection (ECD)[4] and mass spectrometry (MS),[5] high-performance liquid chromatography (HPLC) with ultraviolet (UV) spectroscopy,[6] HPLC-MS[7] and capillary electrophoresis (CE)[8] have been commonly used for the separation and detection of CPs. Moreover, several kinds of pretreatment techniques have been applied to enrich the trace level of CPs, such as solid-phase extraction (SPE),[9] solid-phase microextraction (SPME),[10] stir-bar sorptive extraction (SBSE)[11] and dispersive liquid-liquid microextraction (DLLME).[12] Amongst these techniques, SPE is widely used because of its high-extraction efficiency, the use of a low amount of organic solvent and its easy to automate feature. For SPE, the property of packed adsorbents is the

[a]*School of Light Industry and Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, China. E-mail: whlu@qlu.edu.cn*
[b]*CAS Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai 264003, China. E-mail: lxchen@yic.ac.cn*
[c]*Center for Ocean Mega-Science, Chinese Academy of Sciences, Qingdao 266071, China*
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dominant parameter affecting the extraction efficiency. Nowadays, several kinds of adsorbents have been applied for the extraction of CPs, such as, C18, graphene,[13] carbon nanotubes (CNTs),[14] molecularly imprinted polymers (MIPs)[15] and metal–organic frameworks (MOFs).[16] However, some drawbacks have been reported, such as complicated operating steps of traditional SPE and the difficult synthesis process of adsorbents. Therefore, it is necessary to develop a rapid, simple and effective SPE technique and to synthesize adsorbents with excellent adsorption performance for CPs by a simple preparation process.

Recently, the magnetic solid-phase extraction (MSPE) technique using magnetic materials as adsorbents has received wide attention. Magnetic adsorbents were directly dispersed into the aqueous sample for the extraction of the target analyte and separated by applying an external magnetic field; this method showed a rapid mass transfer rate and a simple separation procedure without filtration and centrifugation. So far, many kinds of magnetic materials have been synthesized and applied in the environmental and biological fields and the food industry, including metals (Fe, Co, Ni), metal oxides ($Fe_3O_4$, $\gamma$-$Fe_2O_3$), and magnetic composite materials.[17–19] To achieve excellent extraction capability, solvent tolerance, biocompatibility and magnetic properties, magnetic composites consisting of magnetic substances ($Fe_3O_4$), inorganic materials ($SiO_2$, carbon-based materials), organic materials (polymers, resin) or biomass materials (chitosan, cellulose) have been commonly synthesized. Amongst these materials, multiwalled carbon nanotubes (MWCNTs) with a large specific surface area, low mass density, unique dimensional structure and high stability have already been applied to synthesize magnetic composites for the removal or extraction of organic/inorganic pollutants.[20–22] For instance, in our previous study, magnetic nanoparticle–multiwalled carbon nanotube composites were prepared by one-pot solvothermal synthesis and applied for the highly efficient removal of Cr(VI) from aqueous solution, where 1,6-hexanediamine functionalized magnetic $Fe_3O_4$ nanoparticles were linked to carboxylic MWCNTs.[23] Masoum *et al.* synthesized MWCNT-based magnetic molecularly imprinted polymers (MWCNT-MMIPs) and applied them as ultrasound-assisted dispersive solid-phase microextraction (UA-DSPME) sorbents for the selective extraction and enrichment of sotalol (SOT) in biological fluid samples. The preparation procedure of MWCNT-MMIPs contains three steps, including the preparation of $Fe_3O_4$ by the chemical co-precipitation method, surface modification of MWCNTs with carboxylic acid groups, and the synthesis of MWCNT-MMIPs by free-radical polymerization.[24] Although the selectivity of MSPE was improved, the problems of poor hydrophilicity and complicated preparation steps still needed to be solved.

Since mussel-inspired polydopamine (PDA) was first reported in 2007, it has attracted wide attention and found broad application, and it can be easily coated on almost all types of inorganic and organic substrates by spontaneous self-polymerization of dopamine under alkaline conditions with oxygen as the oxidant.[25] PDA coating has been proven to have abundant functional groups (catechol, amine and imine), excellent hydrophilicity, good biocompatibility and environmental stability.[26] Moreover, it also offers a large number of active sites for binding metal ions and organic compounds by coordination or chelation, electrostatic interaction, $\pi$–$\pi$ interaction, hydrogen bonding and covalent reactions.[26] Considering the above-mentioned advantages of MSPE, MWCNTs, PDA and the structural properties of CPs, in this study, hydrophilic polydopamine-coated magnetic MWCNT (M-MWCNT) composites were synthesized in two facile preparation steps, including the preparation of M-MWCNTs by solvothermal synthesis and surface modification by self-polymerization of dopamine, and were used as adsorbents for MSPE combined with HPLC for the extraction and fast separation of five typical CPs from water samples. The as-prepared magnetic composites were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), vibrating sample magnetometry (VSM) and thermogravimetric analysis (TGA). The parameters influencing the MSPE extraction efficiency were also investigated in detail, including sample volume and pH, the amount of PDA-coated M-MWCNTs, the type and volume of desorption solvent and desorption time. The validated MSPE–HPLC method showed good linearity, accuracy and precision and was successfully applied to analyze real water samples.

## Experimental

### Reagents and materials

Ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), ethylene glycol (EG), polyethylene glycol 4000 (PEG-4000), anhydrous sodium acetate (NaAc), tris(hydroxymethyl)aminomethane hydrochloride (Tris), HPLC grade formic acid and acetic acid (HAc) were all obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Carboxyl-functionalized multiwalled carbon nanotubes (O.D. 20–30 nm, length 0.5–2 μm) were supplied by Chengdu Organic Chemistry Co., Ltd (Chengdu, China). Dopamine hydrochloride (98%) was purchased from Aladdin (Shanghai, China). HPLC grade reagents 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,6-dichlorophenol (2,6-DCP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) were obtained from Sigma-Aldrich (Shanghai, China). HPLC grade acetonitrile (ACN) and methanol (MeOH) were purchased from J&K Scientific (Shanghai, China).

Throughout the study, ultrapure water with the specific resistance of 18.2 MΩ cm was produced using the Pall Cascada™ lab water purification system (Pall Corp., USA) and was used for the preparation of aqueous solution. All other solvents and chemicals were of analytical grade and used directly without further purification.

### Instrumentation

The analyses of CPs were performed on an Agilent 1260 Infinity HPLC system (Agilent Technologies, Palo Alto, CA,

USA) equipped with a diode array detector (DAD). All five kinds of CPs were separated in a reversed phase column (Agilent ZORBAX SB-C18, 150 × 4.6 mm i.d., particle size 5 μm) in gradient elution mode using the mobile phase consisting of ultrapure water (containing 0.05% formic acid) and acetonitrile at a flow rate of 1 mL min$^{-1}$. The gradient programs were as follows: 0–7 min, 35%–50% acetonitrile; 7–13 min, 50% acetonitrile. The detection wavelength was set as 280 nm for 2-CP, 4-CP and 2,6-DCP and 294 nm for 2,4-DCP and 2,4,6-TCP. The injection volume and column temperature were set as 20 μL and 30 °C, respectively.

For characterization of the as-prepared composite materials, a scanning electron microscope (SEM, Hitachi S-4800, Japan) and a transmission electron microscope (TEM, JEM-2100F, Japan) were used for morphological evaluation. Before SEM observation, the samples were sputter coated with gold. For TEM observation, the samples were uniformly dispersed into ultrapure water by ultrasonication and added dropwise onto the copper grid. X-ray diffraction (XRD-7000, Shimadzu, Japan) measurements were performed using a copper anode generating Cu-Kα radiation ($\lambda$ = 1.5406 Å) at ambient temperature. A Fourier transform infrared (FT-IR) spectrometer (Thermo Nicolet Corporation, USA) with a wavenumber from 500 to 4000 cm$^{-1}$ was employed for the obtaining the infrared spectra of the samples using a pressed KBr tablet. A thermal analyzer (Mettler 5MP/PF7548/MET/400 W, Mettler Toledo, Switzerland) was used to test the thermal stability under a nitrogen atmosphere from 40 to 1000 °C with a flow rate of 50 mL min$^{-1}$ and a heating rate of 20 °C min$^{-1}$. Magnetic properties were analysed using a vibrating sample magnetometer (VSM, LakeShore 7410, USA) with the applied field sweeping from −10000 to 10 000 Oe at room temperature.

### Preparation of PDA-coated M-MWCNTs

**Preparation of M-MWCNTs.** Magnetic multiwalled carbon nanotube composites were synthesized by the solvothermal method; briefly, 1.35 g of FeCl$_3$·6H$_2$O, 3.60 g of anhydrous sodium acetate and 4.00 g of PEG-4000 were firstly dispersed into 40 mL of ethylene glycol by ultrasonication and thoroughly dissolved at 60 °C for 30 min. Then, 100 mg of carboxyl-functionalized MWCNTs were added and uniformly dispersed into the above solution by sonicating for 60 min. After cooling to room temperature, the homogeneous black mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 200 °C for 10 h. When the reaction finished and the autoclave cooled, an Nd–Fe–B permanent magnet was used to collect M-MWCNTs. The obtained M-MWCNTs were individually washed three times using ultrapure water and absolute ethanol to remove the solvent and unreacted reagents and finally dried under vacuum at 40 °C for 12 h.

**Preparation of PDA-coated M-MWCNTs.** The oxidative self-polymerization of DA was used for the preparation of PDA coating. 200 mg of the as-prepared M-MWCNTs were adequately dispersed into 100 mL of Tris-HCl buffer solution (pH = 8.5, 10 mmol L$^{-1}$) by ultrasonication, followed by 200 mg of dopamine hydrochloride. Then, the mixture solution was stirred for 12 h at room temperature. The composites were separated using an Nd–Fe–B permanent magnet and individually washed three times with ultrapure water and methanol. After drying at 40 °C for 12 h, the PDA-coated M-MWCNTs were finally obtained. The whole preparation procedure is briefly shown in Fig. 1A.

### MSPE procedure and sample preparation

The obtained PDA-coated M-MWCNTs were used as sorbents for MSPE to extract five kinds of CPs (2-CP, 4-CP, 2,6-DCP, 2,4-DCP and 2,4,6-TCP) from water samples, and the procedures are shown in Fig. 1B. 30 mg of PDA-coated M-MWCNTs and 30 mL of an aqueous solution containing CPs at the concentration of 50 μg L$^{-1}$ were added into a 50 mL centrifuge tube and sufficiently blended by ultrasonication. Then, the tube was placed in a vibrator spinning at 160 rpm for 30 min to make CPs fully adsorb onto the adsorbents, followed by separation using an Nd–Fe–B permanent magnet. The adsorbents were collected and transferred into a 1.5 mL centrifuge tube after drying. 250 μL of methanol/acetic acid (99 : 1, v/v) was used to desorb CPs from adsorbents by ultrasonication for 8 min. After separation with a magnet, the desorption solvent was filtered through a 0.22 μm Nylon filter and transferred into the sample vial for HPLC analysis.

In order to evaluate the reusability of PDA-coated M-MWCNTs for MSPE, 300 mg of adsorbents first used for MSPE were collected, and subsequently fully desorbed with methanol/acetic acid (99 : 1, v/v), washed with methanol and ultrapure water to neutrality and dried at 40 °C for 12 h. Then, the regenerated adsorbents were reused for the next MSPE procedure, which was marked as cycle 1. The above MSPE–regeneration–MSPE cycle was repeated several times using the same PDA-coated M-MWCNT adsorbents.

Four kinds of real water samples were collected and used for analysis: tap water from our laboratory, lake water from an artificial lake located in Yantai city (China), river water from downstream of Guangdong River located in Yantai city (China) and natural seawater from Yellow Sea located in the coastal zone area of Yantai city (China). All water samples were collected when needed and filtered through a 0.22 μm hydrophilic polypropylene filter membrane to remove the possible suspended impurities before MSPE.

## Results and discussion

### Preparation and characterization of PDA-coated M-MWCNTs

The PDA-coated M-MWCNTs were synthesized in two simple steps, including the preparation of M-MWCNTs and surface modification by self-polymerization of dopamine. As illustrated in Fig. 1A, magnetic Fe$_3$O$_4$ nanoparticles formed by reduction reactions between FeCl$_3$ and EG were firstly decorated on the surface of MWCNTs using solvothermal synthesis. Then, in a weak alkaline environment (pH = 8.5) with oxygen as the oxidant, dopamine can spontaneously self-polymerize. Meanwhile, PDA coating was formed on the surface of
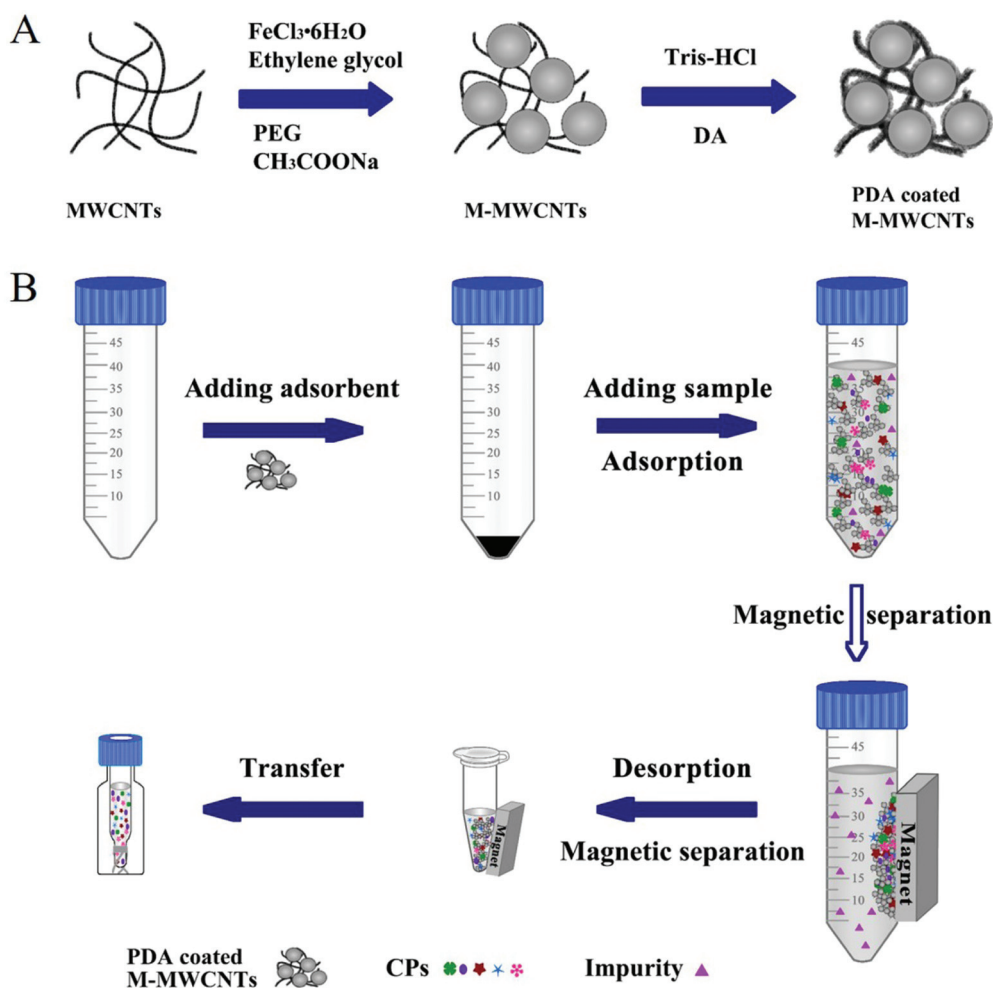
Fig. 1 Schematic procedures for the preparation of PDA-coated M-MWCNTs (A) and magnetic solid-phase extraction (B).

MWCNTs and $Fe_3O_4$ by the π–π stacking interaction between dopamine and MWCNTs,[27] and the formation of –COO–$NH_2$– ion pairs was observed between the carboxyl groups of $Fe_3O_4$ and the amine groups of dopamine.[28] As shown in Fig. 2, SEM and TEM were used to observe the morphological structures of M-MWCNTs (A and B) and PDA-coated M-MWCNTs (C and D). It can be seen that monodisperse $Fe_3O_4$ nanoparticles were attached on MWCNTs because of the addition of NaAc during the solvothermal synthesis procedure (images A and B). NaAc was used for electrostatic stabilization to prevent the nanoparticle agglomeration and assist the EG-mediated reduction of $FeCl_3$ to $Fe_3O_4$.[29] After the second modification step, thin and adherent PDA coatings were successfully formed on the surface of MWCNTs and $Fe_3O_4$ nanoparticles (images C and D).

FT-IR was used to evaluate the structure of MWCNTs and PDA-coated M-MWCNTs, and the results are shown in Fig. 3. For carboxylic MWCNTs (curve A), peaks at 1720 and 1631 $cm^{-1}$ were ascribed to the stretching vibration of C=O and the asymmetric stretching vibration of $COO^-$ from the car-boxylic group.[30] And the peaks at 1079 and 1377 $cm^{-1}$ could be assigned to the C–O–C and C–OH stretching vibrations.[31] From curve B, the bands at around 3422, 1577 and 1494 $cm^{-1}$ were attributed to the aromatic O–H stretching vibration, C=C stretching vibration and CH bending vibration.[32,33] The peaks at 1427 and 1284 $cm^{-1}$ were derived from the N–H scissoring vibration and the C–O–H asymmetric bending vibration from PDA.[30,32,33] The typical absorption peak at around 580 $cm^{-1}$ was attributed to the Fe–O stretching vibration. These results proved that $Fe_3O_4$ was attached to MWCNTs and a PDA coating was formed.

The XRD patterns of MWCNTs and PDA-coated M-MWCNTs are shown in Fig. 4. For curve A, the diffraction peak at $2\theta = 25.96°$ could be indexed to the characteristic (002) for the reflection of MWCNTs.[34] For curve B, the relatively intense diffraction peaks at $2\theta = 30.22°$, 35.62°, 43.18°, 53.68°, 57.04° and 62.74° indexed to (220), (311), (400), (422), (511) and (440) were six characteristic peaks of $Fe_3O_4$.[35] These XRD patterns confirmed that well-crystalline $Fe_3O_4$ was successfully grafted on the surface of MWCNTs.

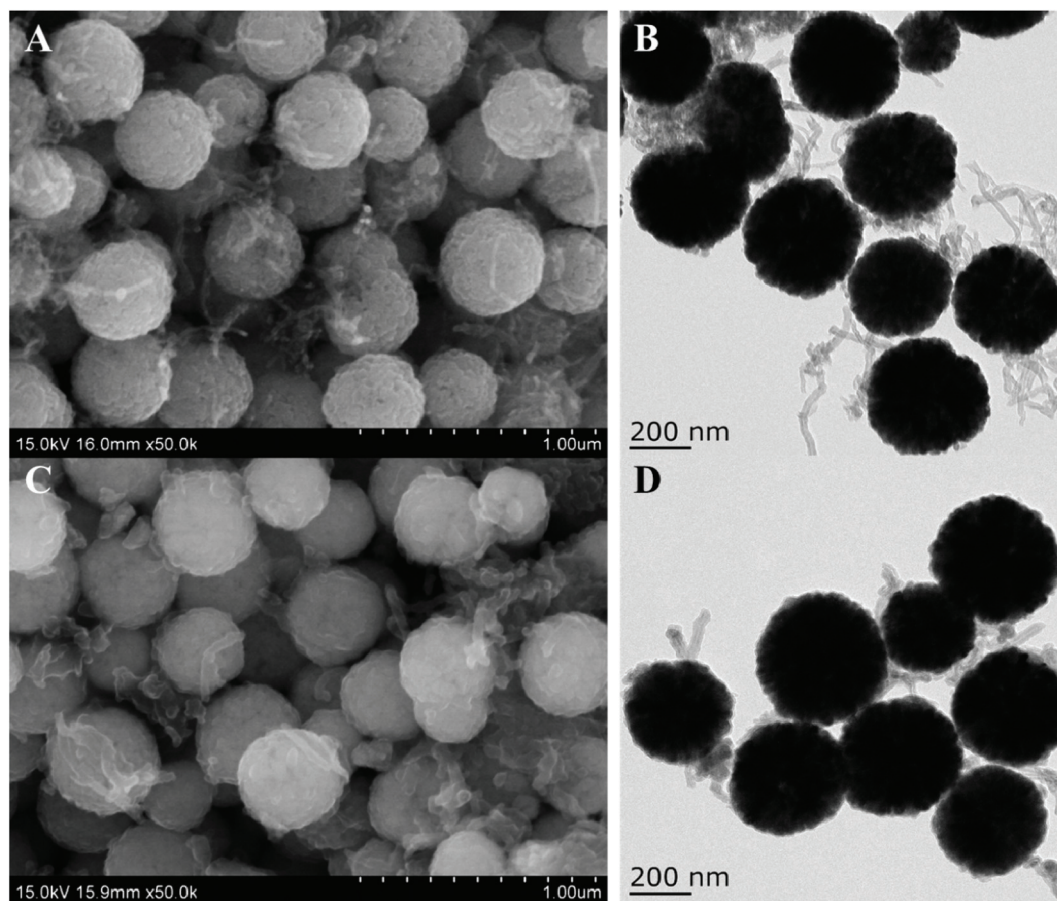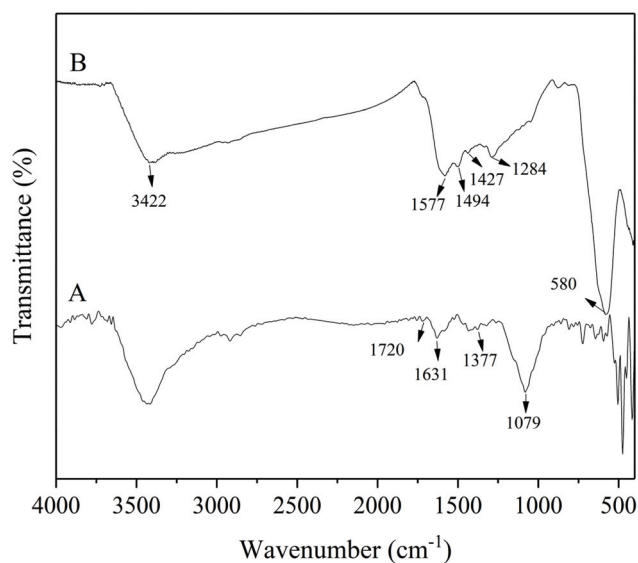Fig. 2   SEM and TEM images of M-MWCNTs (A and B) and PDA-coated M-MWCNTs (C and D).



Fig. 3   FT-IR spectra of MWCNTs (A) and PDA-coated M-MWCNTs (B).



Fig. 4   XRD patterns of MWCNTs (A) and PDA-coated M-MWCNTs (B).

For the application of PDA-coated M-MWCNTs as disperse adsorbents, magnetic properties are an important index to evaluate the separation efficiency from aqueous solution.[36]
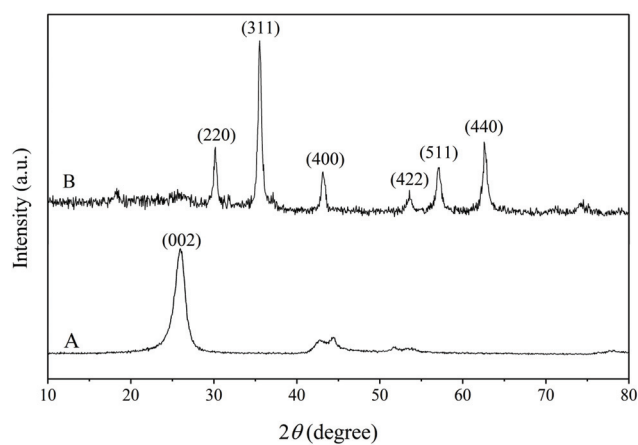
The magnetic properties of M-MWCNTs and PDA-coated M-MWCNTs were analysed by VSM at room temperature. The magnetic hysteresis loops and magnetic parameters obtained from the hysteresis loops are shown in Fig. S1 and Table S1.† As observed from Fig. S1,† excellent magnetic properties for both M-MWCNTs and PDA-coated M-MWCNTs were observed,

and the shapes of the magnetization curves had no obvious difference after the PDA coating. As presented in Table S1,† the attained values of saturation magnetization ($M_s$), residual magnetization ($M_r$) and coercivity ($H_c$) for the PDA-coated M-MWCNTs were slightly lower than those for the M-MWCNTs, indicating that the PDA coating was formed on the surface of M-MWCNTs.

The thermal stability of the M-MWCNTs and PDA-coated M-MWCNTs was evaluated by thermogravimetric analysis. As shown in Fig. S2,† for M-MWCNTs (curve A), no obvious change from 40 to 380 °C and a high rate of weight loss of about 21.77% from 380 to 600 °C were observed, which might be attributed to the desorption of $Fe_3O_4$ from MWCNTs. For PDA-coated M-MWCNTs (curve B), firstly, the weight decreased slightly from 40 to 200 °C (about 2.77%), and then a continuous slow weight loss of about 10.07% occurred from 200 to 450 °C, which might be related to the thermal decomposition of the PDA coating. From 450 to 620 °C, the weight loss of about 18.17% can also be ascribed to the desorption of $Fe_3O_4$. Thus, the prepared PDA-coated M-MWCNTs can be used at a temperature lower than 200 °C.

### Condition optimization of the MSPE procedure

The proposed PDA-coated M-MWCNTs were used as adsorbents for MSPE coupled with HPLC-DAD for the simultaneous extraction and analysis of five kinds of CPs in aqueous solution. Several main factors affecting the extraction efficiency of MSPE were investigated and optimized in detail, including the sample volume and pH, the amount of PDA-coated M-MWCNTs, and the type and volume of desorption solvent and desorption time. Moreover, the reusability of PDA-coated M-MWCNTs for MSPE was also investigated. The whole experiments were performed in triplicate using the standard solution containing 2-CP, 4-CP, 2,6-DCP, 2,4-DCP and 2,4,6-TCP with the concentration of 50 μg L$^{-1}$.

Sample volume can influence the enrichment factor (EF) and the equilibrium time of extraction of CPs. Different sample volumes of 10, 20, 30 and 40 mL were investigated, and the results are shown in Fig. 5A. For 2-CP and 4-CP, the extraction efficiency had no obvious change with the increase of sample volume. For 2,6-DCP, 2,4-DCP and 2,4,6-TCP, the extraction efficiency continuously increased with the sample volume from 10 mL to 30 mL. When the sample volume was increased to 40 mL, the extraction efficiency of 2,6-DCP and 2,4-DCP reached equilibrium, and the extraction efficiency still increased for 2,4,6-TCP. Considering that four kinds of CPs can show high extraction efficiency and a larger sample volume might increase the difficulty of wastewater treatment, 30 mL of sample was chosen for further experiments. Moreover, the sample pH was also investigated based on the acid or base properties of CPs and their water solubility. The sample pH values from 4.0 to 9.0 (interval 1.0) adjusted with 1 mol L$^{-1}$ HCl or 1 mol L$^{-1}$ NaOH were used for the evaluation. As shown in Fig. 5B, for five kinds of CPs, the extraction efficiency slightly increased at pH 4.0–7.0 and decreased at alkaline pH. The results were possibly ascribed to the molecular form of CPs and the binding interaction between the PDA coating and CPs. The p$K_a$ values of 2-CP, 4-CP, 2,6-DCP, 2,4-DCP and 2,4,6-TCP are 8.3–8.6, 9.1–9.4, 6.7–7.8, 7.5–8.1 and 6.0–7.4, respectively.[37] At neutral pH, most of the CPs exist in the molecular state, and can bind with the PDA coating by π–π stacking interaction and hydrogen bonding. At basic pH, CPs exist in the ionic state and might show electrostatic repulsion with the negatively charged PDA coating. Therefore, 30 mL of sample (pH = 7.0) was used for the MSPE procedure.

The effect of different amounts of PDA-coated M-MWCNTs from 15 mg to 35 mg (interval 5 mg) was evaluated. As shown in Fig. 5C, the extraction efficiency of five kinds of CPs increased from 15 mg to 30 mg and reached optimization at 30 mg and equilibrium at 35 mg, indicating that 30 mg of PDA-coated M-MWCNTs were sufficient for the extraction of CPs from aqueous solution. Moreover, large amounts of adsorbents needed a large volume of desorption solvent for wetting which can decrease the volume concentration factor. 30 mg of PDA-coated M-MWCNTs were used for further study.

Desorption is the crucial step in MSPE for fully releasing the adsorbed CPs from the PDA-coated M-MWCNTs. Several parameters including the kind and volume of desorption solvent and desorption time were investigated. Firstly, acetonitrile, methanol, and methanol containing 1%, 5% and 10% acetic acid (v/v) were chosen as desorption solvents. As shown in Fig. 5D, methanol showed a better desorption efficiency than acetonitrile, and the addition of acetic acid in methanol can improve the release of CPs from the PDA-coated M-MWCNTs. However, with the increase of acetic acid concentration, certain decrease of desorption efficiency was observed, possibly because the hydrogen bond between the carboxyl group of acetic acid and CPs decreased. Therefore, methanol containing 1% acetic acid (v/v) showed an optimum desorption efficiency. Moreover, the volume of methanol containing 1% acetic acid (v/v) ranging from 200 to 500 μL was investigated. As shown in Fig. 5E, the desorption efficiency for five kinds of CPs decreased with the increase of volume. Although the optimum data were obtained at 200 μL, more exhausting assays were needed, because more or less volume loss occurred when 200 μL of methanol containing 1% acetic acid (v/v) was filtered through a syringe filter before the HPLC analysis. If the residual volume lowers than the required volume of the autosampler, HPLC cannot work, so the same volume needed to be experimented many times to obtain useful data. Compared with 200 μL, 250 μL was easy to handle and showed enough extraction efficiency. Based on this, 250 μL of methanol containing 1% acetic acid (v/v) was used for the further study. Ultrasonication was chosen to desorb CPs from the PDA-coated M-MWCNTs, and the desorption time was investigated in the range of 3–15 min. The results are shown in Fig. 5F. The desorption efficiency increased with ultrasonication from 3 min to 8 min, reached the optimum value at 8 min, and then tended to equilibrium, indicating that 8 min
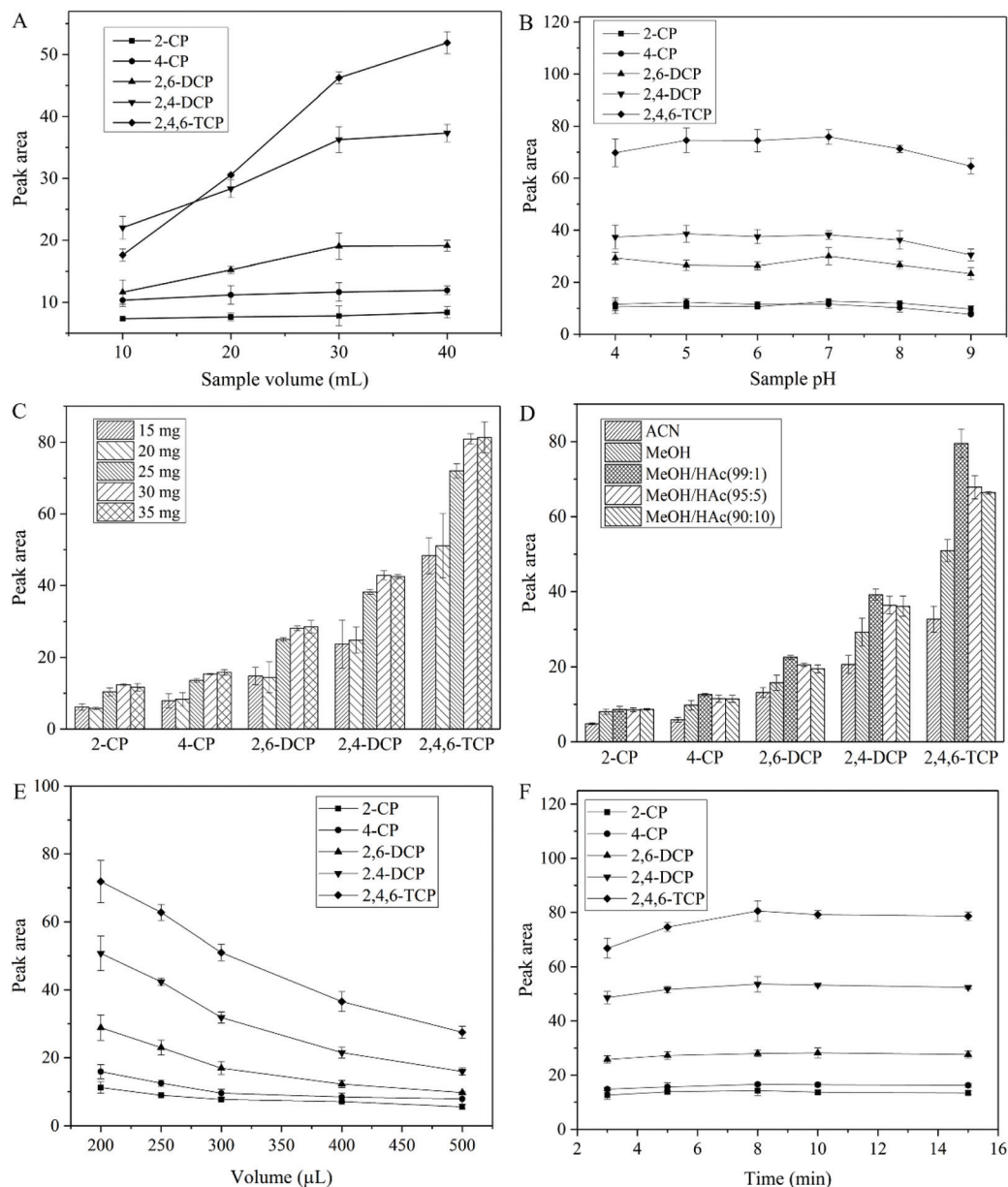
**Fig. 5** Optimization of the MSPE procedure. The effect of sample volume (A), sample pH (B), the amount of PDA-coated M-MWCNTs (C), the type of desorption solvent (D), the volume of desorption solvent (E) and desorption time (F). Extraction conditions: (A) 20 mg PDA-coated M-MWCNTs; sample pH, 7.0; 160 rpm shaking for 30 min; 250 μL methanol/acetic acid (90 : 10, v/v) and sonication for 5 min; (B) sample volume, 30 mL; other conditions as (A); (C) sample pH, 7.0; other conditions as (B); (D) 30 mg PDA-coated M-MWCNTs; other conditions as (C); (E) desorption solvent, methanol/acetic acid (99 : 1, v/v); other conditions as (D); (F) desorption solvent volume, 250 μL; other conditions as (E).

was sufficient to desorb the retained CPs from the PDA-coated M-MWCNTs. Accordingly, the optimal desorption conditions were set as using 250 μL of methanol containing 1% acetic acid (v/v) to desorb in 8 min by ultrasonication.

The reusability of the PDA-coated MWCNTs for MSPE was investigated by MSPE–regeneration–MSPE experiment. As shown in Fig. S3,† the peak areas of CPs showed no significant decrease after five MSPE–regeneration–MSPE cycles using the same adsorbents. Considering that methanol containing 1% acetic acid was used in the desorption step of MSPE, it was

confirmed that the PDA-coated MWCNTs are stable in an acidic environment and organic solvent.

### Method performance and practical application of MSPE–HPLC

Under the optimum MSPE conditions, a series of solutions containing five kinds of CPs with different concentrations were extracted and used to evaluate the analytical performance of this proposed MSPE–HPLC method, and the results are presented in Table 1. Good linearity was obtained in the range of 2.0–200 μg L$^{-1}$ for 2-CP and 4-CP and 1.0–200 μg L$^{-1}$ for 2,6-

**Table 1**  Analytical performances of the MSPE–HPLC method for the determination of five kinds of CPs

| CPs | Calibration curves[a] | Correlation coefficient ($R^2$) | Linear range ($\mu g\ L^{-1}$) | LOD ($\mu g\ L^{-1}$) | LOQ ($\mu g\ L^{-1}$) | Intraday precision[b] (RSD, %) | Interday precision[b] (RSD, %) | EF[b] |
|---|---|---|---|---|---|---|---|---|
| 2-CP | $y = (0.258 \pm 0.00583)x + (1.05 \pm 0.570)$ | 0.9964 | 2.0–200 | 0.31 | 1.03 | 1.61 | 1.88 | 85 |
| 4-CP | $y = (0.272 \pm 0.00533)x + (3.17 \pm 0.495)$ | 0.9969 | 2.0–200 | 0.18 | 0.61 | 1.05 | 2.11 | 93 |
| 2.6-DCP | $y = (0.543 \pm 0.00926)x + (1.84 \pm 0.821)$ | 0.9974 | 1.0–200 | 0.28 | 0.94 | 2.08 | 2.83 | 89 |
| 2.4-DCP | $y = (0.852 \pm 0.0126)x + (3.25 \pm 1.17)$ | 0.9983 | 1.0–200 | 0.10 | 0.35 | 1.95 | 2.27 | 112 |
| 2,4,6-TCP | $y = (1.01 \pm 0.0103)x + (5.84 \pm 0.915)$ | 0.9991 | 1.0–200 | 0.17 | 0.56 | 2.25 | 2.66 | 98 |

[a] $y$ and $x$ stand for the peak area and the concentration ($\mu g\ L^{-1}$) of all the analytes, respectively. [b] Intraday precision ($n = 5$), interday precision ($n = 5$) and EF were calculated at the concentration of 50 $\mu g\ L^{-1}$ individually for all the analytes.

DCP, 2,4-DCP and 2,4,6-TCP, with the correlation coefficient ($R^2$) higher than 0.9964. The limits of detection (LODs) and limits of quantification (LOQs) calculated based on the signal-to-noise ratio (S/N) of 3 and 10 were in the range of 0.10–0.31 $\mu g\ L^{-1}$ and 0.35–1.03 $\mu g\ L^{-1}$, respectively. The intra-day and interday precisions evaluated from the relative standard deviation (RSD) were calculated via five replicate analyses at the same day and five different days at the concentration of 50 $\mu g\ L^{-1}$ for all the analytes. The RSD values ranged from 1.05–2.25% and 1.88–2.83%, respectively, indicating that the method was highly accurate and reliable. The enrichment factor (EF) is defined as the ratio between the concentration of the analyte after MSPE and the initial concentration. The calculated EFs were obtained in the range of 85–112, showing a relatively high pretreatment efficiency. As shown in Fig. 6, the peak area and peak height showed a significant increase for all five kinds of CPs after MSPE, which also indicated excellent enrichment efficiency.

The feasibility and practical applicability of the validated MSPE–HPLC method were further assessed by the analysis of real water samples, including tap water, lake water, river water and seawater samples. The endogenous CPs were not detected in the four water samples, owing to their quite low concentrations in complicated matrices. The recoveries of four real water samples spiked in five kinds of CPs at the concentration of 5 and 10 $\mu g\ L^{-1}$ treated by MSPE–HPLC were investigated and the results are presented in Table 2. Satisfactory recoveries were obtained in the range of 80.31–93.02% with RSDs of 1.84–5.55% for tap water, 76.87–99.26% with RSDs of 2.40–6.48% for lake water, 77.33–86.20% with RSDs of 1.64–6.35% for river water and 78.21–106.5% with RSDs of 2.08–6.78% for seawater. These results confirmed that the developed MSPE–HPLC method is practically applicable for the analysis of traces of chlorophenols in water samples.

### Method performance comparison

The analytical performances of this validated method were compared with those of the other reported MSPE–HPLC methods for the analysis of CPs in water samples, as presented in Table S2.† As seen from the table, for the preparation of magnetic materials, $Fe_3O_4$ synthesized by the solvothermal method and chemical coprecipitation method is commonly used as a core or support material and also a time-consuming preparation procedure (three or more steps) is needed.[38–42]
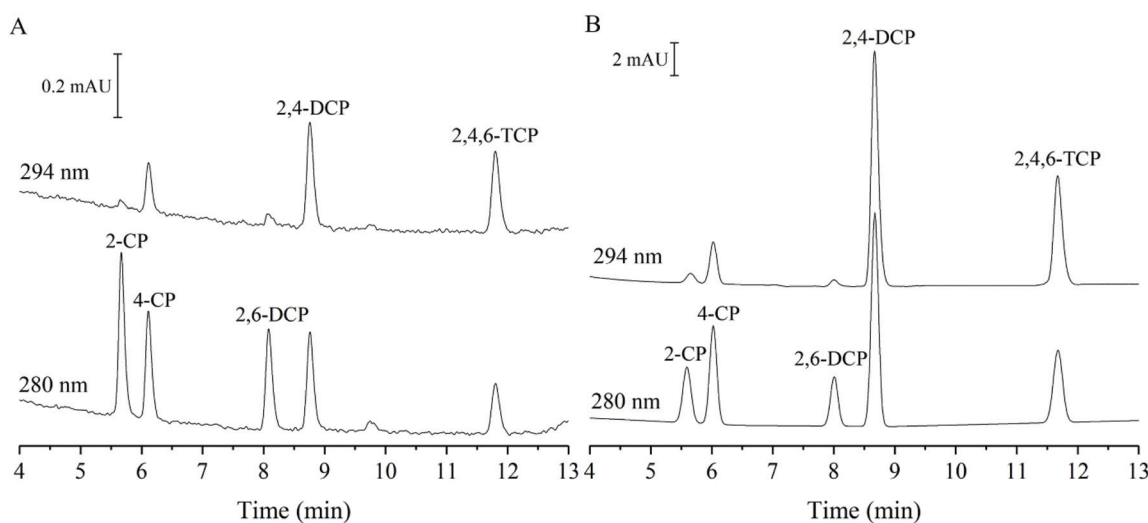
**Fig. 6**  Chromatograms of five kinds of CPs in standard solution monitored at 280 and 294 nm with the concentration of 200 $\mu g\ L^{-1}$ (A) and 50 $\mu g\ L^{-1}$ after MSPE (B). HPLC conditions: mobile phase, ultrapure water (containing 0.05% formic acid) and acetonitrile; gradient programs, 0–7 min, 35%–50% acetonitrile; 7–13 min, 50% acetonitrile; flow rate, 1 mL min$^{-1}$; injection volume, 20 $\mu$L; column temperature, 30 °C.

**Table 2** Results of the recovery study of five kinds of CPs spiked in four real water samples by the developed MSPE–HPLC method ($n = 3$)

| CPs | Spiked ($\mu g\ L^{-1}$) | Tap water | | | Lake water | | | River water | | | Seawater | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Average ± SD ($\mu g\ L^{-1}$) | Recovery (%) | RSD (%) | Average ± SD ($\mu g\ L^{-1}$) | Recovery (%) | RSD (%) | Average ± SD ($\mu g\ L^{-1}$) | Recovery (%) | RSD (%) | Average ± SD ($\mu g\ L^{-1}$) | Recovery (%) | RSD (%) |
| 2-CP | 5.0 | 4.13 ± 0.10 | 82.58 | 2.45 | 4.22 ± 0.21 | 84.49 | 4.89 | 3.87 ± 0.16 | 77.33 | 4.18 | 4.18 ± 0.12 | 83.54 | 2.97 |
| | 10.0 | 8.64 ± 0.25 | 86.42 | 2.93 | 7.69 ± 0.36 | 76.87 | 4.66 | 7.81 ± 0.25 | 78.06 | 3.24 | 8.16 ± 0.41 | 81.65 | 5.06 |
| 4-CP | 5.0 | 4.09 ± 0.21 | 81.72 | 5.05 | 4.06 ± 0.23 | 81.24 | 5.66 | 4.15 ± 0.13 | 82.91 | 3.05 | 4.21 ± 0.20 | 84.10 | 4.84 |
| | 10.0 | 9.21 ± 0.25 | 92.12 | 2.74 | 8.62 ± 0.36 | 86.16 | 4.15 | 8.14 ± 0.51 | 81.39 | 6.21 | 8.38 ± 0.55 | 83.78 | 6.52 |
| 2,6-DCP | 5.0 | 4.04 ± 0.22 | 80.74 | 5.53 | 4.18 ± 0.10 | 83.52 | 2.40 | 3.89 ± 0.12 | 77.74 | 3.16 | 4.03 ± 0.16 | 80.51 | 3.91 |
| | 10.0 | 8.05 ± 0.23 | 80.53 | 2.80 | 8.98 ± 0.35 | 89.78 | 3.87 | 8.02 ± 0.13 | 80.18 | 1.64 | 7.82 ± 0.53 | 78.21 | 6.78 |
| 2,4-DCP | 5.0 | 4.39 ± 0.24 | 87.76 | 5.55 | 4.70 ± 0.20 | 94.00 | 4.31 | 4.31 ± 0.17 | 86.20 | 3.84 | 3.94 ± 0.08 | 78.79 | 2.08 |
| | 10.0 | 9.30 ± 0.18 | 93.02 | 1.92 | 9.93 ± 0.33 | 99.26 | 3.33 | 7.98 ± 0.31 | 79.76 | 3.88 | 10.2 ± 0.40 | 101.8 | 3.89 |
| 2,4,6-TCP | 5.0 | 4.02 ± 0.20 | 80.31 | 5.08 | 4.87 ± 0.32 | 97.31 | 6.48 | 3.88 ± 0.25 | 77.69 | 6.35 | 5.32 ± 0.21 | 106.5 | 3.91 |
| | 10.0 | 8.29 ± 0.15 | 82.92 | 1.84 | 8.36 ± 0.39 | 83.64 | 4.69 | 8.01 ± 0.16 | 80.11 | 1.97 | 9.15 ± 0.29 | 91.49 | 3.22 |

Our PDA-coated M-MWCNTs synthesized by the solvothermal method with two simple preparation steps showed a homogeneous morphology, uniform size, good monodispersity and magnetic properties. Compared with the reported $Fe_3O_4@SiO_2$ and magnetic porous carbon-based MSPE–HPLC method, this proposed method showed adequately low LODs, high accuracy and practical applicability, which can meet the needs of the analysis of CPs in water samples.

## Conclusions

In the present work, polydopamine-coated magnetic MWCNT composites were prepared by a solvothermal method and simple surface modification and were used as magnetic solid phase extraction sorbents to simultaneously extract and enrich five kinds of chlorophenols in aqueous solution, followed by HPLC analysis. PDA-coated M-MWCNTs synthesized by a simple preparation procedure showed excellent magnetic properties, and can be rapidly separated from aqueous solution by applying an external magnetic field and they simplify the extraction process when used as an MSPE adsorbent. This proposed MSPE–HPLC method showed satisfactory linearity, sensitivity and accuracy, and was successfully applied to four real water samples with recoveries from 76.87 to 106.5%. Moreover, given the advantages of this method and the summary of the reported MSPE–HPLC methods for the analysis of chlorophenols, further research should focus on developing a simple and efficient preparation method to synthesize magnetic materials with high adsorption capacity, selectivity and magnetic performance, which can simultaneously extract and enrich many kinds of CPs at trace levels in complicated matrices.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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