A new, rapid, green, and cost-effective magnetic solid-phase extraction of ochratoxin A from red wine samples was developed using polydopamine-coated magnetic multi-walled carbon nanotubes as the absorbent. The polydopamine-coated magnetic multi-walled carbon nanotubes were fabricated with magnetic multi-walled carbon nanotubes and dopamine by an in situ oxidative self-polymerization approach. Transmission electron microscopy, dynamic light scattering, X-ray photoelectron spectroscopy and vibrating sample magnetometry were used to characterize the absorbents. Ochratoxin A was quantified with high-performance liquid chromatography coupled with fluorescence detection, with excitation and emission wavelengths of 338 and 455 nm, respectively. The conditions affecting the magnetic solid-phase extraction procedure, such as pH, extraction solution, extraction time, absorbent amount, desorption solution and desorption time were investigated to obtain the optimal extraction conditions. Under the optimized conditions, the extraction recovery was 91.8–104.5% for ochratoxin A. A linear calibration curve was obtained in the range of 0.1–2.0 ng/mL. The limit of detection was 0.07 ng/mL, and the limit of quantitation was 0.21 ng/mL. The recoveries of ochratoxin A for spiked red wine sample ranged from 95.65 to 100.65% with relative standard deviation less than 8%. The polydopamine-coated magnetic multi-walled carbon nanotubes showed a high affinity toward ochratoxin A, allowing selective extraction and quantification of ochratoxin A from complex sample matrices.

**KEYWORDS**
magnetic carbon nanotubes, magnetic solid-phase extraction, ochratoxin A, polydopamine, red wine

### 1 | INTRODUCTION

Ochratoxin A (OTA) is a toxic secondary metabolite belonging to methylisocoumarin derivatives, which is mainly produced by several mold fungi in the genus of *Aspergillus* and *Penicillium* [1–4]. It may cause severe risks in human beings such as embryotoxicity, teratogenicity, carcinogenicity, nephrotoxicity, immunotoxicity and hepatotoxicity [5]. Moreover, it is metabolized in biological body very slowly [6]. OTA exists in a wide range of food stuffs from barley, oats, rye, wheat, coffee beans, to many other plant products [7–12]. Wine is one of the most widely produced and consumed beverages across the world, while it is also the second main source of OTA intake for the population [13,14]. European Committee (EC) has established the maximum limitation for OTA in
wine at 2 μg/kg [15], and the Food and Drug Administration (FDA) of the United States has approved the limits of 50 ppb in foods and 1000 ppb in feeds [16]. Therefore, it is important to develop a rapid, simple, sensitive and cost-effective method for quantitative determination of OTA.

Several methods for separation and enrichment of OTA have been developed such as ELISA [17,18], molecularly imprinted sorbents [19], liquid–liquid microextraction (LLE) [20], immunoaffinity chromatography (IAC) [21] and SPE [22,23]. ELISA is likely to produce false positives due to the interfering components [24], and the molecular imprinted sorbents need complex synthetic routes [25]. The IAC possesses high selectivity and specificity, but it needs expensive IAC columns, and quite a lot of factors (salts, pH and organic solution) can cause irreversible denaturation of antibodies to shorten the life of the columns. In comparison, SPE has more advantages such as simple operation and low solution consumption [21]. In recent years, magnetic solid-phase extraction (MSPE) with different superparamagnetic nanoparticles absorbents has been widely used due to the high surface area-to-volume ratio, high extraction efficiency, easy separation and rapid extraction kinetics [26]. Magnetic multi-walled carbon nanotubes (mCNTs) combine the advantages of magnetic properties and CNT’s strong absorptive ability towards organic molecules for its extremely large surface areas and great conjugated π–π system; therefore, they exhibit promising applications in MSPE. The mCNTs have been reported to extract type A trichothecenes and nerve agents from complex samples [27,28]. However, mCNTs are not good enough as SPE absorbents because they are apt to aggregate in solvents. On the other hand, dopamine is a good agent for solid surface modification due to its ability to form surface-adherent polydopamine films by self-polymerization onto various materials including noble metals, oxides, semiconductors, ceramics and synthetic polymers [29]. The polydopamine modification approach is simple, convenient and environmental friendly [30], thus increasingly attempts have been made to modify magnetic SPE absorbents in this way to improve extraction ability. For example, dopamine-coated magnetic nanoparticles have been applied for the enrichments of berberine from traditional Chinese medicine [31], polycyclic aromatic hydrocarbons in water samples [32], and aflatoxins in red wine [33]. These studies further evidenced that dopamine modified materials have great potential to absorb the compounds with good planarity. The phenyl group of dopamine can provide π–π stacking interaction to target compounds, while the amino and hydroxyl groups can provide hydrogen bonding and ionic interaction. However, there have no reports on the synthesis and application of dopamine-coated (PD) mCNTs until now. Thus, PD-mCNTs can be expected to be an excellent adsorbent for the MSPE of OTA.

In this work, we developed a rapid, sensitive, cost-effective, and environmental friendly method using mCNTs coated with polydopamine as a solid phase absorbent for HPLC–FLD determination of OTA in red wine. PD-mCNTs were synthesized and characterized with TEM, DLS, XPS, VSM and CV. The experimental parameters affecting the extraction efficiency such as absorbent amount, pH, adsorption time, eluting solvents and desorption time were investigated, and the analytical characteristics of the method were evaluated. To the best of our knowledge, this is the first time that PD-mCNTs were synthesized and applied for the enrichment of OTA. Finally, real red wine samples were analyzed to demonstrate the applicability of the proposed method.

2 MATERIALS AND METHODS

2.1 Reagents and standard solution

OTA was purchased from Sigma–Aldrich (St. Louis, USA). Dopaamine hydrochloride was supplied by J&K scientific (Beijing, China). Multi-walled carbon nanotubes with 20–40 nm in diameter were purchased from Shenzhen Nanotech Port (Shenzhen, China). Ferrous chloride (FeCl3·6H2O), sodium dihydrogen phosphate (NaH2PO4), sodium hydroxide (NaOH), trisodium citrate (Na3C6H5O7), methanol (MeOH), acetonitrile (ACN), potassium chloride (KCl), potassium ferricyanide (K3[Fe(CN)6]), sodium acetate (CH3COONa), trihydroxymethyl aminomethane (Tris), hydrochloric acid (HCl) and poly (ethylene glycol) with average molecular weight of 2000 were purchased from Chengdu Tianhua Chemical Technology (Chengdu, China). The HPLC grade methanol for HPLC was obtained from Fisher Scientific (Fairlawn, USA). HPLC grade water was produced by a MilliQ (18.2 M) system (Millipore, Bedford, USA). A standard solution containing 1.0 mg/mL of OTA was prepared with methanol and stored at −20°C until use. The work standard solutions were prepared daily by appropriate dilution with methanol/water (5:95, v/v).

2.2 Apparatus

The mCNTs and PD-mCNTs were characterized using TEM (FEI Tecnai G220, USA), dynamic light scattering (DLS; SZ-100, Japan), vibrating sample magnetometry (VSM; MPMS-S3, USA), X-ray photoelectron spectroscopy (XPS; Thermo Scientific K-Alpha, USA), and cyclic voltammetry (CV; Gaoss Union EC500, China). The HPLC analysis was performed with Shimadzu LC-20AD (Shimadzu, Japan), coupled with an RF-5301 PC fluorescence spectrophotometer equipped with a 12 μL flow cell (Shimadzu, Japan) for fluorescence detection (FLD). A COSMOSIL (COSMOSIL, Japan) packed C18 column (4.6 × 150 mm, 5 μm) with guard column (4.6 × 10 mm) was used for separation.
2.3 | Preparation of polydopamine coated-magnetic carbon nanotubes

mCNTs were prepared by a one-pot hydrothermal procedure according to previously reported method with minor modification [34]. Firstly, 400 mg of primitive multi-walled carbon nanotubes were dispersed into 50 mL of concentrated nitric acid by vigorously stirring at 60°C for 7 h to obtain the oxidized CNTs. The oxidized CNTs were rinsed with distilled water for several times until the pH value reached neutral and then dried with vacuum freeze dryer. Secondly, 200 mg of the oxidized CNTs and 810 mg of FeCl₃·6H₂O were dispersed into 40 mL of ethylene glycol solution under ultrasonication for 2 h. After that, 150 mg of trisodium citrate, 3.6 g of sodium acetate, and 1.0 g of poly(ethylene glycol) were added with constant stirring for 1 h. The mixture was then transferred into a Teflon-lined autoclave to heated at 200°C for 10 h. Then, the product of mCNTs was washed with ethanol and deionized water and then dried with vacuum freeze dryer. Polydopamine coated mCNTs (PD-mCNTs) were prepared by mCNTs and dopamine by an oxidative self-polymerization approach with minor modification [35,36]. Forty milligrams of mCNTs were dispersed in 8 mL of buffer solution (pH 8.5) with 10 mM trihydroxymethyl aminomethane-hydrochloric acid buffer. A total of 20 mg of dopamine hydrochloride was then added to the mCNTs suspension to be vigorously stirred overnight. After the reaction, the resultant PD-mCNTs were isolated with a magnet and washed with distilled water for several times. The final products were dispersed into 4 mL of deionized water and kept at 4°C for further use. The preparation of PD-mCNTs was illustrated in Fig. 1A.

2.4 | MSPE of ochratoxin A

A total of 60 μL of the PD-mCNTs suspension prepared above was added into a conical flask containing 50 mL of OTA in MeOH/PBS (5:95) solution at concentration of 1.0 ng/mL. The mixture was shaken for 15 min on an oscillator to let PD-mCNTs absorb OTA and the magnetic particles were then isolated from the solution with an external magnet. After washing the PD-mCNTs three times with MeOH/PBS (5:95), OTA was eluted with 500 μL of ACN (pH 3.3). The eluent was filtered through a 0.22 μm filtration membrane for the subsequent HPLC analysis. The mobile phase is consisted of 1% ammonium hydroxide in water (A) and methanol (B). The column was eluted with 60% B at a flow rate of 0.6 mL/min, and the retention time for OTA was found at 3.0 min. The excitation and emission wavelength for fluorescent detection were 338 and 455 nm, respectively. The MSPE process is illustrated in Fig. 1B.

2.5 | Method validation

The method was validated for linearity, LOD and LOQ, true-ness and precision.

2.5.1 | Linearity, LOD and LOQ

The linearity of the method was estimated by analyzing different standard OTA solutions with concentrations of 0.1, 0.4, 0.8, 1.0, and 2.0 ng/mL. These solutions were submitted to the MSPE procedure before HPLC–FLD analysis. Peak areas were used for the calculation of linear equation. The LOD and LOQ were determined by referring to the US EPA standard.

FIGURE 1  (A) Illustration of the preparation of PD-mCNTs; (B) Illustration of the proposed MSPE procedure for facile extraction of ochratoxin A followed by HPLC–FLD quantification
Briefly, a laboratory standard at a concentration four times of the estimated method detection limit was prepared, and tested for seven times. The LOD and LOQ were then calculated according to the following equations [37]:

\[
\text{LOD} = t_{0.99} \times S \\
\text{LOQ} = 3 \times \text{LOD}
\]

Where \( S \) is the SD of the replicate analyses, and \( t_{0.99} \) is the Student \( t \) value at the 99% confidence level, which is 3.143 in this work due to seven times of test were carried out.

### 2.5.2 Trueness and precision

The extraction recovery (\( R \)) was calculated according to the following equation:

\[
R = \left( \frac{C_0}{C_s} \right) \times 100\%
\]

Where \( C_0 \) is the obtained concentration (ng/mL) of OTA and \( C_s \) is the added concentration (ng/mL) of OTA.

### 3 RESULT AND DISCUSSION

#### 3.1 Characterization of polydopamine coated-magnetic carbon nanotubes

The mCNTs and PD-mCNTs were characterized by TEM, DLS, XPS, CV and VSM. The morphology and size of the synthesized polydopamine coated mCNTs absorbents were obtained by TEM. As shown in Fig. 2, the particle sizes of mCNTs and PD-mCNTs were both around 100–200 nm. However, due to the good water-solubility of the PD-mCNTs introduced by polydopamine, there is less agglomeration for PD-mCNTs than the mCNTs. As shown in Fig 3A, the mCNTs precipitated much faster than the PD-mCNTs, while the latter could be well kept for at least one week. The DLS spectra of PD-mCNTs and mCNTs in Fig. 3B and C showed that the average hydrodynamic radius of them were 544 and 420 nm, respectively. Compared to the mCNTs, the PD-mCNTs possess plenty of amino and hydroxyl groups and thus resulting in bigger hydrodynamic radius. Therefore, it was evidenced that polydopamine has been successfully immobilized onto the mCNTs.

The composition of the PD-mCNTs was characterized with XPS as shown in Fig. 3D. The spectra shows photoelectron lines at binding energies of about 284.5, 530.4, 400.7 and 711.3 eV, which can attributed to C 1 s, O 1 s, N 1 s and Fe 2p, respectively. The photoelectron peaks at 711.3 and 724.2 eV were ascribable to Fe 2p3/2 and 2p1/2, respectively. The absence of satellite peaks at the 716–720 eV indicated that the mCNTs were Fe3O4-MWCNTs [38,39]. In addition to the peaks for C, O and Fe, the peak at 400.7 eV for N 1s indicated that polydopamine was successfully coated on the surface of mCNTs.

Magnetic properties of mCNTs and PD-mCNTs were measured with VSM at room temperature. As shown in Fig. 3E, both mCNTs and PD-mCNTs nanoparticles exhibited superparamagnetism and the saturation magnetizations were 54.08 and 43.93 emu/g, respectively. The saturation magnetization of the PD-mCNTs is smaller than that of mCNTs, indicating that nonmagnetic polydopamine was coated on the mCNTs. Nevertheless, like the mCNTs, the PD-mCNTs can be easily separated from the solution with an external magnet, and re-dispersed rapidly when the magnet was taken away. Therefore, the PD-mCNTs can be used as an excellent magnetic adsorbent for MSPE.

In the cyclic voltammetry (CV), the immobilization of nano-composite on electrodes usually results in a change of...
FIGURE 3  (A) The image of PD-mCNTs (left) and mCNTs (right) disperse in water. (B) DLS of the mCNTs; (C) DLS of the PD-mCNTs; (D) XPS spectra of the PD-mCNTs nanoparticles; (E) Magnetization curves of the mCNTs and PD-mCNTs nanoparticles; (F) CV of the electrode at difference stages: bare-screen printed carbon electrode (1), mCNTs (2), and PD-mCNTs (3). Supporting electrolyte: pH 7 PBS containing 5 mM FeCN(K$_3$Fe(CN)$_6$) and 0.1 M KCl; scan rate: 50 mV/s. Carbon rings served as the working and counter electrodes, Ag/AgCl reference electrode.

current response; therefore, CV has usually been used to characterize the nano-composite [40,41]. In this work, the cyclic voltammograms of mCNTs and PD-mCNTs were measured in phosphate buffer (PBS) (pH 7) containing 0.1 M KCl and 5 mM potassium ferricyanide. The mCNTs or PD-mCNTs was suspended in PBS at a concentration of 10 mg/mL, and then 10 μL of the suspension was added into the reaction pool of screen-printed carbon electrode with an external magnet placed under the electrode so that the magnetic particles can be immobilized onto the electrode's surface. The potential range was set from −0.2 to 0.6 V at a scan rate of 50 mV/s. A comparison of CV signals of bare electrode,
mCNTs and PD-mCNTs is shown in Fig. 3F. A couple of stable and well-defined redox peaks were observed in curve (1) for the bare electrode, and the peak potentials corresponding to the redox of $[\text{Fe(CN)}_6]^{4-/-3^{-}}$ anions were 132 and 248 mV, respectively. The peak current of mCNTs represented by curve (2) is significantly higher than that of the bare electrode of curve (1), which is due to the better conductivity of the mCNTs. However, the peak current for PD-mCNTs of curve (3) decreased significantly compared to mCNTs, indicating that the insulative polydopamine was successfully immobilized onto the mCNTs to decrease the electron-transfer efficiency of $[\text{Fe(CN)}_6]^{4-/-3^{-}}$.

### 3.2 Comparison of extraction efficiency of magnetic carbon nanotubes and polydopamine coated magnetic carbon nanotubes

To compare the extraction efficiency of mCNTs and PD-mCNTs, 60 μL of each nano-composite was added respectively to 50.0 mL of OTA in MeOH/PBS (5:95) solution at a concentration of 1.0 ng/mL. As shown in Fig. 4, the extraction recovery of PD-mCNTs was 99.4%, which was significantly higher than 13.8% for the mCNTs. PD-mCNTs exhibited dramatically stronger affinity towards OTA, which might be due to the $\pi-$ $\pi$ stacking interaction provided by the phenyl groups in PD-mCNTs, as well as the hydrogen bonding and ionic interaction provided by the amino and the hydroxyl groups of PD-mCNTs. Therefore, PD-mCNTs can be expected to be an excellent absorbent for the MSPE of OTA.

### 3.3 Effects of pH and extraction solvent

Both the amino groups in PD-mCNTs and the carboxyl groups in OTA are ionizable groups, thus the pH value will significantly affect the MSPE process. The $pK_a$ value of the carboxyl group in OTA is 4.4, while the $pK_b$ value of the amino group of PD-mCNTs was 9 to 10. Based on acid–base theory, carboxyl group takes anionic form and amino group cationic form when pH value is between 4.4 and 10. At a very low pH, the ferromagnetic materials can be dissolved or oxidized [22]. Therefore, pH values from 5 to 9 were tested in this work. As shown in Fig. 5A, the best performance of pH was 7, at which nearly 99.2% of OTA was extracted. On the other hand, 5, 10, and 20% of MeOH in PBS buffer, together with pure MeOH and pure PBS buffer were tested for extraction of OTA. The best absorption for OTA was found in 5% of MeOH as shown in Fig. 5B.

### 3.4 Effects of the amount of polydopamine coated-magnetic carbon nanotubes

To investigate the effects of the amount of PD-mCNTs on extraction efficiency, a series of suspensions containing different amounts of PD-mCNTs (10, 20, 40, 60, 80, 100, and 200 μL) were added respectively to 50.0 mL of OTA in MeOH/PBS (5:95) solution at concentration of 1.0 ng/mL. The extraction recovery of OTA increased from 17.2 to 96.2% when the amount of the absorbent increased from 10 to 60 μL, while remained nearly constant at 96.2% when > 60 μL of PD-mCNTs suspension was used. Therefore, 60 μL of PD-mCNTs was selected for the following experiment.

### 3.5 Effects of the shaking rate and extraction time

To investigate the effect of shaking rate, 100, 200, 300, 400, and 500 r/min were tested for as shown in Fig. 6A. The recoveries between 93.1 and 97.6% showed that shaking rates have no obvious effect on the SPE procedure of OTA. On the other hand, extraction time of 2, 5, 10, 15, 20, and 30 min were tested. As shown in Fig. 6B, it is found that the PD-mCNTs was so efficient that the extraction recovery reached to 80.7% within only 2 min, with the maximum one in 15 min. Therefore, 15 min was selected as the extraction time for further studies.

### 3.6 Desorption solvent and desorption time

To fully elute the OTA from the adsorbents, the use of appropriate desorption solvent is important. According to the literatures, the desorption solvent should be acidified to around pH 3.3 [13,42]. So we chose pH 3.3 in this experiment. The MeOH, ACN, MeOH/ACN (50:50), ACN/acetate buffer (50:50) and pure acetate buffer were tested for their desorptive abilities for OTA absorbed in PD-mCNTs. The ACN was found to be the most effective desorption solvent to retrieve OTA from PD-mCNTs as shown in Fig. 6C. In the meantime, the desorption time of 1, 2, 3, 5, and 10 min were tested as shown in Fig. 6D. The desorption efficiency increased with the elapse of time before 3 min, while decreased after that time.
which was probably due to the degradation of OTA under acid condition. Therefore, the best desorption time was 3 min.

### 3.7 Method validation

Based on the above experimental results, the optimal condition for the MSPE of OTA with PD-mCNTs was selected as following: PD-mCNTs amount: 60 μL; sample volume: 50 mL; sample pH value: 7.0; extraction solution: MeOH/PBS (5:95); extraction time: 15 min; desorption solution: acid acetonitrile (pH 3.3); desorption volume: 500 μL; elution time: 3.0 min. The method was evaluated under the optimized condition. The regression equation was $Y = 0.44246X + 0.08559$ ($r^2 = 0.995$). The LOD and LOQ
TABLE 1 Comparison of analytical methodologies for OTA determination

| Detection Method | Technique    | Enrichment Factor | LOQ (ng/mL) | Time | References |
|------------------|--------------|-------------------|-------------|------|------------|
| HPLC-FLD         | MSPE         | 100               | 0.21        | 15 min | This work  |
| HPLC-FLD         | on-line SPE  | 1                 | 0.1         | 10 min | [42]       |
| HPLC-FLD         | LMPE         | 80                | 0.25        | 2 h   | [13]       |
| HPLC-FLD         | Immunoaffinity column | 40 | 0.05 | N.A. | [43] |
| UPLC-MS          | HF-LPME      | 8                 | 0.02        | 4 h   | [44]       |
| HPLC-MS          | QuEChERS     | 5                 | 0.4         | 10 min | [45]       |
| HPLC-MS          | QuEChERS     | 0.25              | 1           | 10 min | [46]       |
| HPLC-QTOF-MS     | reversed-phase SPE | 40 | 0.05 | 15 min | [7] |

N.A. not available, LPME: liquid phase micro extraction.

were calculated to be 0.07 and 0.21 ng/mL, respectively. The recovery rates were between 91.8 and 104.6%, and the RSDs were 3.2–4.6% for the intra-days and 4.5–5.6% for the inter-days.

The proposed MSPE method was compared to certain previously reported ones in Table 1. Those methods include QuEChERS, reversed-phase SPE techniques combined with HPLC–MS and HPLC–QTOF-MS. It is noted that a greater enrichment factor and a relatively shorter extraction time were achieved with this method, and the sensitivity remained in the same order with those reported studies. Therefore, our method can be used to enrich and quantitatively detect OTA in alcohol liquid.

3.8 Sample analysis

According to the optimized extraction conditions obtained above, the red wine purchased from local market was diluted with PBS buffer to adjust the alcoholicity from 13.8% to around 5%, and the pH was adjust to 7.0 with NaOH. The OTA was spiked into the wine at low, medium and high concentration levels and the recoveries of 95.6 to 100.6% are summarized in Table 2, with RSDs less than 8%. In addition, the chromatogram of the extracted OTA (Fig. 7) showed that OTA peak was not interfered by other matrix components, indicating that the method can be used to detect OTA in red wine.

4 CONCLUSIONS

The polydopamine-coated magnetic multi-walled carbon nanotubes (PD-mCNTs) were firstly synthesized with mCNTs and dopamine by a facile oxidative self-polymerization approach. The PD-mCNTs composite exhibited excellent properties including great absorptive ability, high stability and good dispersibility, making it an ideal absorbent for MSPE. Under the optimized MSPE conditions, PD-mCNTs showed dramatically high affinity to OTA. Based on this newly prepared MSPE absorbent, we developed a simple, rapid, sensitive and cost-effective analytical method for OTA coupled with HPLC–FLD. Furthermore, this method has been applied in the analysis of OTA in wine with good sensitivity,
showing promising potential in the enrichment and quantification of OTA and its analogues present in a wide range matrix.

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