Three-dimensional graphene aerogel-supported iron oxide nanoparticles as an efficient adsorbent for magnetic solid phase extraction of organophosphorus pesticide residues in fruit juices followed by gas chromatographic determination

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ABSTRACT

In this research, a magnetic three dimensional-graphene nanocomposite (3D-G-Fe₃O₄) was prepared, characterized and used as an effective nanoadsorbent in magnetic solid-phase extraction (MSPE) of eight organophosphorus pesticides (OPPs) from juice samples prior to gas chromatography-nitrogen-phosphorous detection (GC-NPD). The properties and morphology of 3D-G-Fe₃O₄ were characterized by scanning electron microscopy (SEM), Fourier transform-infrared spectroscopy (FT-IR) and vibrating sample magnetometry (VSM). The main experimental parameters affecting extraction recoveries including extraction time, amount of adsorbent, pH of sample solution, salt concentration and desorption conditions were carefully studied and optimized. The results showed wide linear concentration ranges with determination coefficients between 0.9973 and 0.9999. The limits of detection (S/N = 3) of the method and limits of quantification (S/N = 10) were from 1.2 to 5.1 ng L⁻¹ and 3.4–17.0 ng L⁻¹, respectively. The intra-day and inter-day RSDs were 2.6–5.1% and 3.5–6.9%, respectively. The method was successfully applied to the analysis of OPPs in fruit juices (apple, orange, grape, sour-cherry and apricot) with recoveries in range of 86.6–107.5%. The GC-NPD results were confirmed by gas chromatography–mass spectrometry (GC–MS). The results demonstrated that with combination of highly interconnected 3D network structure and magnetism property of adsorbent, 3D-G-Fe₃O₄ aerogel exhibited exceptional extraction ability towards the OPPs.

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1. Introduction

Carbon based nanomaterials are well known for their high adsorption capacity for various compounds and thus they have been widely used as adsorbents over the past decades [1]. Graphene (G) is a relatively new type of carbon nanomaterial which is made of a single-atom-thick, two-dimensional sp² carbon network in a honeycomb lattice [2]. In recent years, this material has attracted the attention of many researchers due to its extraordinary electrical and thermal conductivity, high specific surface area, and large mechanical strength [3]. In addition, large delocalized π-electron system of graphene can form a strong hydrophobic and π–π stacking interactions with different molecules, so G and G-based materials are good candidates for use as adsorbent in sample preparation techniques [4–16].

However, recent studies have shown that the restacking and aggregation between individual graphene sheets caused by the strong π–π stacking, hydrophobic interactions, and van der Waals forces may greatly decrease the intrinsic high specific surface area of G, which is undesirable for its applications. In order to solve this problem, the reassembly of two-dimensional graphene (2D-G) sheets into three-dimensional graphene (3D-G) structures such as aerogels, sponges and foams has gained remarkable interest in the last few years [17–20]. Compared with 2D-G, the 3D structures provide materials with higher specific surface area, lower density, stronger mechanical strength, and faster mass and electron transport kinetics due to combination of 3D interconnected framework and excellent intrinsic properties of G [21].

These unusual properties of 3D-G provide it with great application potential in many fields. To date, 3D-G structures have been mainly used in super capacitors [22–24], sensors [25,26], batteries [27] and catalysis [28]. The ultrahigh surface area, porous and hollow structure of 3D-G, and fast mass transport kinetics, make it a promising candidate for an efficient adsorbent. However, the
application of 3D-G as an adsorbent for extraction or removal of chemical pollutants is still not deeply studied [21,29–32].

Within the past few years, much effort has been paid to the development of strategies for preparing 3D-G structures and compositions of graphene with other materials such as polymers, carbon nanotubes and metal oxides [18,33]. A simple approach for fabrication of a three-dimensional graphene-based magnetic nanocomposite (3D-G-Fe₃O₄) is the self-assembly of reduced graphene oxide nanosheets by ferrous ions and in situ simultaneous deposition of Fe₃O₄ nanoparticles [34]. The magnetic 3D-G combines the ultrahigh adsorption capacity of 3D-G and the separation convenience of magnetic materials, which makes it an ideal adsorbent for different compounds in sample preparation techniques especially magnetic solid phase extraction (MSPE) procedures. In MSPE, as a new mode of solid phase extraction (SPE), the magnetic adsorbent can be dispersed directly in the sample solution and the phase separation can occur simply by using an external magnet without any need to filter or centrifuge samples, making separation easier and faster [35].

Organophosphorus pesticides (OPPs) are some of the most common and most toxic insecticides widely used today for pest control in agriculture and public places [36]. They can easily leach or migrate into various environments during their usage [37]. Certain OPPs as well as their metabolites and degradation products can cause adverse effects on human health even at low levels of exposure [38]. Fruits and vegetables are among the foods most commonly contaminated with OPPs. The European Union has established maximum residue limits (MRL) for pesticide residues in many vegetables and fruits in the range of 0.01–0.3 mg kg⁻¹ and 0.01 mg kg⁻¹ for pesticide residues in processed foods [39]. Therefore, developing rapid, sensitive and simple analytical methods to detect OPPs residue in different matrices have become a major research focus.

The main aim of this work was to evaluate the performance of 3D-G-Fe₃O₄ as an efficient adsorbent for extraction of OPPs. Therefore, the as-fabricated adsorbent was used for the MSPE of eight OPPs (azinphos methyl, parathion methyl, fenitrothion, methidathion, ethion, phosalone, phorate and coumaphos) in different fruit juices. The OPPs residue levels were determined by GC–NPD, and the residues were verified by GC–MS. The factors affecting the extraction recoveries were carefully investigated and the related optimized values were obtained. This is the first report of application of magnetic 3D-G as an adsorbent for the extraction of OPPs in fruit juices.

2. Experimental

2.1. Reagents and materials

Acetonitrile, acetone, hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium chloride (NaCl), ferric chloride hexahydrate (FeCl₃·6H₂O), ferrous sulfate heptahydrate (FeSO₄·7H₂O), ammonia solution (NH₃, 25%) and all other reagents were prepared from Merck Chemicals (Darmstadt, Germany). Methanol (MeOH) was obtained from Sigma Aldrich Ltd. (St Louis, USA). Pesticide standards (azinphos methyl, parathion methyl, fenitrothion, methidathion, ethion, phosalone, phorate and coumaphos) were purchased from Beijing Chemical Reagents Company (Beijing, China). A mixture stock standard solution containing each OPP at 50.0 mg L⁻¹ was prepared in acetone and was stored at 4 °C in dark. Working solutions were prepared daily by appropriate dilutions with water.

2.2. Instrumentation

An Agilent technologies 7890 gas chromatograph (Santa Clara CA, USA) equipped with a nitrogen-phosphorus detector (NPD) and a split/splitless injector was applied for quantitative analysis of the extracted OPPs. All the separations were performed on a HP-5 capillary column (30 m × 0.32 mm i.d.; 0.25 μm, film thickness; 5% phenyl-95% methyl polysiloxane) (Agilent Scientific, USA) with helium (>99.999%) as carrier gas at the flow-rate of 1.0 mL min⁻¹. The GC chromatographic conditions were as follows: splitless mode; injector temperature, 250 °C; detector temperature,
290 °C; the column oven temperature program: started at 100 °C for 1 min, then increased to 180 °C at 50 °C min⁻¹, and raised to 200 °C at the rate of 5 °C min⁻¹ and finally ascended to 270 °C at 50 °C min⁻¹ held for 8 min. The total analysis run time was 16 min.

The GC–MS analyses were performed using a 6890 GC system equipped with a 5973 network mass selective detector (Agilent 161 Technologies, Santa Clara, CA, USA) and a HP5-MS capillary fused silica with 5% phenyl-95% polydimethylsiloxane (30 m 0.25 mm i.d., 0.25 μm film thickness). The oven temperature program was the same as GC–NPD conditions. The injector and auxiliary temperatures were 250 and 290 °C, respectively. Mass spectra were taken at 70 eV ionization energy and full scan mode. An enhanced ChemStation software package (G1701 DA-MSD, Rev. D.00.01.27) was used for the data collection and analysis in GC–MS.

The FT-IR spectra were obtained on an Equinox 55 FT-IR spectrometer (Bruker, Bremen, Germany) using KBr discs. The morphology of the 3D–Fe₃O₄ was observed by scanning electron microscopy (SEM) with a KYKY-EM3200 machine (KYKY, Beijing, China). The magnetic properties of the adsorbent were studied using a vibrating sample magnetometer (VSM/AGFM Meghnatis Daghigh Kavir Co., Kashan, Iran) at room temperature. A vortex mixer model ZX-Classic (Velp Scientifica, Milan, Italy) was used for stirring the solutions to help desorption of OPPs from the adsorbent.

2.3. Synthesis of 3D-G-Fe₃O₄

Graphene oxide (GO) was prepared according to the method in our previous work [40]. 3D-G-Fe₃O₄ was synthesized by a vacuum freeze-dried method [34]. Typically, 0.695 g FeSO₄·7H₂O was added into a 50 mL aqueous suspension of GO at the concentration of 2 mg mL⁻¹, under sonication for 5 min. The sample pH was then adjusted to 11 with 25% NH₃·H₂O, and the resulting suspension was then heated at 90 °C for 6 h in an oil bath without stirring. The reduced graphene oxide sheets anchored with nanoparticles were simultaneously self-assembled into the 3D hydrogel with interconnected networks driven by combined hydrophobic and π-π stacking interactions, due to the decrease of oxygenated groups on graphene sheets. The resultant 3D-G-Fe₃O₄ hydrogel was separated by filtration and washed with water. The aerogel was placed in a glass vial, which was then transferred to a cold source with constant temperature. Freezing continued for several minutes until the gel was completely solidified. After the gel was fully frozen, the sample was placed in a freeze dryer for 24 h, generating black magnetic 3D-G aerogel. Fig. 1 shows a schematic illustration of the formation mechanism of the 3D-G-Fe₃O₄ aerogel.

Two-dimensional graphene nanocomposite (2D-G-Fe₃O₄) was synthesized according to the method reported by Wang et al.
Fig. 3. Effect of (a) type of desorption solvent; (b) extraction time; (c) adsorbent amount; (d) pH; and (e) salt concentration on the extraction recovery of OPPs.

Briefly, GO nanosheets were reduced to graphene layers by hydrazine solution. The magnetic graphene (2D-G-Fe₃O₄) was then synthesized by in situ chemical coprecipitation of Fe²⁺ and Fe³⁺ in alkaline solution in the presence of G sheets.

2.4. MSPE procedure

The MSPE procedure was consisted of the following main steps: first, 10 mg of 3D-G-Fe₃O₄ was added into 50 mL of sample solution containing OPPs. The mixture was then shaken on a slow-moving platform shaker (300 rpm) for 2 min. Next, the adsorbent was isolated from the aqueous phase by placing a magnet (with 1.3 T magnetic flux density) at the outside bottom of the vial and the supernatant was discarded. The adsorbent was then washed with distilled water and the residual solution was completely removed by a pipette. In the next step, 0.5 mL of acetone/hexane (1:1 v/v) mixture was added to the isolated adsorbent and vortexed for 30 s for desorption of the analytes. The desorption solvent was transferred to a 2 mL micro-centrifuge tube. Same desorption procedures were performed again and the collected desorption solutions were
combined together (total volume of 1 mL) and then evaporated to dryness under nitrogen stream (at 60 °C). Finally, the residue was dissolved in 100 µL acetone, and 1 µL of it was injected into the gas chromatograph for analysis.

3. Results and discussion

3.1. Characterization of the adsorbent

Morphology of 3D-G-Fe₃O₄ was observed by SEM. As can be seen from the SEM image of 3D-G-Fe₃O₄ (Fig. 2a), reduced GO nanosheets were randomly assembled to build a porous and 3D network structure. The image also showed that Fe₃O₄ nanoparticles were distributed in all parts of 3D-graphene structure and anchored onto graphene layers, suggesting an efficient assembly between iron oxide nanoparticles and graphene sheets during the synthesis procedure. The same results were observed by the SEM image of 3D-G-Fe₃O₄ synthesized by Wu et al. [32].

Chemical composition of 3D-G-Fe₃O₄ was analyzed by FT-IR spectrometry. According to the FT-IR spectrum in Fig. 2b, most characteristic features for GO were absorption bands corresponding to C=O stretching vibration at 1734 cm⁻¹, absorption band at 1622 cm⁻¹ attributed to aromatic C=C, C–O characteristic bands at 1220 and 1034 cm⁻¹, and OH broad peak at 3440 cm⁻¹. These results verified the presence of oxygen functional groups on GO nanosheets surfaces. In comparison with the FT-IR spectrum of GO, most of absorption bands attributed to the oxygen functional groups of GO have obviously been decreased in the FT-IR spectrum of 3D-G-Fe₃O₄, indicating effective reduction of graphene sheets in the synthesis process. Meanwhile, the absorption band at 574 cm⁻¹ in the FT-IR spectrum of 3D-G-Fe₃O₄ is the characteristic vibration of Fe–O bond. Thus, the above analyses indicated that the hydrogel was fabricated by co-assembly of graphene sheets and Fe₃O₄ nanoparticles.

The magnetic property of the 3D-G-Fe₃O₄ nanocomposite was characterized using VSM technique at room temperature. Based on the obtained VSM curve at low and room temperatures, magnetic behavior of materials can be identified. For superparamagnetic particles, the magnetization become zero when the external field approached zero. Saturation magnetization (Ms) can also be determined from the plateau part of the VSM curve [42,43]. As can be seen from Fig. 2c, the magnetic hysteresis curve is S-like and passes through the zero point of magnetization with no remanence nor coercivity, suggesting superparamagnetic property of 3D-G-Fe₃O₄. Moreover, a high saturation magnetization amount of 54.8 emu g⁻¹ was observed for adsorbent, reflecting its good magnetic property. This value was lower than that of the bare Fe₃O₄ particles (81.9 emu g⁻¹) as reported in previous literature by Li et al. [44]. The decrease in saturation magnetization of adsorbent can be due to contribution of the nonmagnetic GO layers to the total magnetization. Ma et al. [45] have reported that a saturation magnetization of 16.3 emu g⁻¹ is enough for magnetic separation of particles from solution by a magnet. Thus, the magnetic 3D-G loaded with OPPs can be separated readily from solution (<30 s separation can be achieved) with a permanent magnet due to their superparamagnetism and large saturation magnetization. The pictures in the inset of Fig. 2c shows the apple fruit juice sample before addition of the adsorbent, after addition of the adsorbent, and after placing the magnet on the outside of vial, respectively.

3.2. Optimization of MSPE procedure

To obtain the highest extraction recovery of the magnetic 3D-G, different experimental parameters that may affect the extraction recovery, including desorption conditions (type and volume of desorption solvent), extraction time, amount of the adsorbent, sample solution pH, and ionic strength were carefully investigated and optimized using 50 mL of sample solution containing 5000 ng L⁻¹ of each OPP. All experiments were performed in triplicates and mean values were used for data analysis. The extraction recovery, R%, was calculated based on the following equation (Eq. (1)):

\[
R% = \frac{C_0 \times V_o}{C_{aq} \times V_{aq}} \times 100
\]

where \(C_0\), \(C_{aq}\), \(V_o\) and \(V_{aq}\) are final concentrations of analyte in organic phase (acetone), initial concentration of analyte in aqueous phase, volume of organic solvent (100 µL of acetone), and volume of aqueous phase (50 mL), respectively.

3.2.1. Effect of desorption conditions

In order to obtain a higher desorption efficiency, the most commonly used organic solvents (acetone, acetonitrile and MeOH) were investigated as desorption solvents. The results showed a better extraction recovery was obtained with acetone among the three solvents. However, none of these solvents were successful toward an acceptable desorption of the analytes. This can be due to low or moderate polarity of the investigated OPPs. A mixed solution of polar and nonpolar solvents can facilitate an effective desorption of the analytes. Therefore, a mixed solution of acetone with some nonpolar organic solvents including CH₂Cl₂, toluene, and n-hexane was tested at a ratio of 1:1. As can be seen in Fig. 3a, the mixture of acetone and hexane showed the highest desorption capability towards the OPPs. Therefore, the mixture of acetone and hexane was selected for desorption of OPPs from the adsorbent. Different ratios of acetone and hexane (1:2; 1:1; 2:1 and 4:1 v/v) were also investigated to obtain the optimized value. The results indicated that maximum extraction recoveries were achieved with a 1:1 (v/v) ratio of acetone/hexane. Therefore, the mixture of acetone/hexane was chosen as the desorption solvent.

Effect of the volume of acetone/hexane (1:1 v/v) on the extraction recoveries was also studied. It was found that all the analytes could be desorbed quantitatively from 3D-G-Fe₃O₄ by eluting the adsorbent with 0.5 mL acetone/hexane (1:1 v/v) for two times. Therefore, the total amount of 1 mL (2 × 0.5 mL) of acetone/hexane (1:1 v/v) was chosen for desorption of OPPs. Finally, desorption solutions were combined together (1 mL) in a micro-centrifuge tube and dried under nitrogen stream (at 60 °C). The dried residue
was then dissolved in 100 μL acetone and 1 μL of it was injected into the gas chromatograph.

The experiments showed that vortexing can efficiently facilitate release of the analytes from the adsorbent. Therefore, the effect of vortex time on the extraction recoveries was studied in the range of 0.5–2 min. Results showed that complete desorption of analytes from the adsorbent was achieved very quickly at 0.5 min, and further increasing the vortex time had no significant effect on the extraction recoveries. Therefore, the experiments were performed with vortex time of 0.5 min in the desorption step of analytes.

3.2.2. Effect of extraction time

In general, the MSPE procedure is an equilibrium-based technique and thus, there is a direct relationship between extracted amount of analytes and contact time between the analytes and the adsorbent. Extraction recovery is usually enhanced by increasing the extraction time until an equilibrium is reached. In this work, extraction time was investigated from 0.5 to 5 min to find the optimum analysis time at which highest extraction recovery is obtained. As can be seen in Fig. 3b, maximum extraction recoveries were reached in a very short time of 2 min for all of the OPPs. The obtained very short extraction time is attributed to the ultra large specific surface area of 3D interconnected porous structure of the adsorbent, which provides easy diffusion of analytes to the adsorption sites. Based on this result, 2 min was chosen as the optimum extraction time.

3.2.3. Effect of adsorbent amount

In order to choose the optimum dosage of the adsorbent, different amounts of 3D-G-Fe₃O₄ were investigated in the range of
5–20 mg. The results (Fig. 3c) showed that extraction recoveries for all analytes increased with increasing the amount of the adsorbent from 5 to 10 mg due to higher available sites of adsorbent for interaction with analytes and then remained almost constant. This amount (10 mg) of the adsorbent is far less than traditional SPE sorbents [36], which can be attributed to the ultra-large surface area and high adsorption efficiency of 3D-G-Fe$_3$O$_4$. Hence, 10 mg of 3D-G-Fe$_3$O$_4$ was selected as the optimum amount of adsorbent for all following experiments.

3.2.4. Effect of pH

The pH of the sample solution is a key factor affecting chemical forms of analytes and/or effective surface charge of the adsorbent and as a result, it can change the extraction recovery. Therefore, the pH of the solution should be carefully investigated and optimized. Due to the reduction of oxygen functional groups on surfaces of GO, the surface charge of 3D-G-Fe$_3$O$_4$ is not affected significantly by changing the pH value. Consequently, varying the pH can only change the structure of analytes. To investigate the effect of pH on the extraction recovery of OPPs, the pH of sample solution was adjusted with HCl or NaOH in the range of 3–11 while other experimental conditions were constant. As shown in Fig. 3d, extraction recoveries of OPPs remained constant when the pH was changed from 3 to 9 and after that, extraction recoveries were slightly decreased. This can be due to the hydrolysis of OPPs under alkaline conditions. Therefore, pH of the sample solution should not be...
Table 2
Results for the analysis of the fruit juice samples.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Phorate</th>
<th>Methyl parathion</th>
<th>Fenitrothion</th>
<th>Methidathion</th>
<th>Ethion</th>
<th>Phosalone</th>
<th>Methyl azinphos</th>
<th>Coumaphos</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apple juice</td>
<td>18.6</td>
<td>54.3</td>
<td>36.5</td>
<td>n.d</td>
<td>n.d</td>
<td>20.1</td>
<td>n.d</td>
<td>89.7 (51)</td>
</tr>
<tr>
<td>Grape juice</td>
<td>93.3 (3.2)</td>
<td>87.6 (4.4)</td>
<td>92.1 (2.5)</td>
<td>92.4 (3.0)</td>
<td>95.9 (4.7)</td>
<td>91.9 (2.8)</td>
<td>101.2 (3.5)</td>
<td>97.6 (3.2)</td>
</tr>
<tr>
<td>Orange juice</td>
<td>99.0 (4.6)</td>
<td>104.3 (3.5)</td>
<td>97.2 (5.2)</td>
<td>93.3 (3.2)</td>
<td>106.1 (2.8)</td>
<td>94.4 (4.7)</td>
<td>92.9 (3.2)</td>
<td>93.3 (3.2)</td>
</tr>
<tr>
<td>Sour-cherry juice</td>
<td>100.5 (4.3)</td>
<td>90.2 (2.7)</td>
<td>93.8 (6.2)</td>
<td>96.7 (5.6)</td>
<td>94.5 (3.9)</td>
<td>102.2 (3.4)</td>
<td>89.8 (6.1)</td>
<td>95.0 (2.9)</td>
</tr>
<tr>
<td>Apricot juice</td>
<td>95.1 (5.9)</td>
<td>98.7 (6.5)</td>
<td>86.6 (4.8)</td>
<td>106.4 (6.3)</td>
<td>93.4 (4.1)</td>
<td>94.2 (7.4)</td>
<td>102.3 (5.7)</td>
<td>107.5 (6.3)</td>
</tr>
</tbody>
</table>

Table 3
Comparison of the proposed MSPE method with other SPE-based techniques for determination of OPPs.

<table>
<thead>
<tr>
<th>Method</th>
<th>Adsorbent</th>
<th>Sample</th>
<th>LOD (μg L⁻¹)</th>
<th>LDR (μg L⁻¹)</th>
<th>R² (%)</th>
<th>RSD (%)</th>
<th>tᵢ (min)</th>
<th>Adsorbent (mg)</th>
<th>PF*</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSPE-GC/MS</td>
<td>Fe₃O₄@SiO₂/Co₄</td>
<td>Water</td>
<td>0.005–0.025</td>
<td>0.02–0.6</td>
<td>62.2</td>
<td>86.4</td>
<td>4.4–9.6</td>
<td>30</td>
<td>15</td>
<td>492–965</td>
</tr>
<tr>
<td>MSPE-</td>
<td>Fe₃O₄/MWCNTs</td>
<td>Tea</td>
<td>0.006–0.024</td>
<td>0.08–2.0</td>
<td>72.5</td>
<td>109.1</td>
<td>4.5–12.6</td>
<td>1</td>
<td>100</td>
<td>–</td>
</tr>
<tr>
<td>GC/MS</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MSPE/HPLC-UV</td>
<td>Fe₃O₄/C</td>
<td>Water</td>
<td>0.004–0.047</td>
<td>0.05–0.40</td>
<td>79.6</td>
<td>103.5</td>
<td>3.7–6.6</td>
<td>–</td>
<td>97.4</td>
<td>330–1200</td>
</tr>
<tr>
<td>MSPE/HPLC-UV</td>
<td>Fe₃O₄@SiO₂/Co₄</td>
<td>Water</td>
<td>0.026–0.030</td>
<td>0.1–1.5</td>
<td>88.5</td>
<td>96.7</td>
<td>2.4–8.7</td>
<td>20</td>
<td>100</td>
<td>1000</td>
</tr>
<tr>
<td>MSPE-GC/MS</td>
<td>Fe₃O₄@SiO₂/Co₄</td>
<td>Water</td>
<td>1.8–5.0</td>
<td>10–3000</td>
<td>–</td>
<td>5.4</td>
<td>10.7</td>
<td>10</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>SPE-GC-NPD</td>
<td>MWCNTs</td>
<td></td>
<td>0.04–1.03</td>
<td>0.05–1.68</td>
<td>73</td>
<td>112</td>
<td>2.3–8.5</td>
<td>–</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>SPE-GC/MS</td>
<td>Graphene</td>
<td>Apple juice</td>
<td>0.04–0.13</td>
<td>0.5–200</td>
<td>96.9</td>
<td>106.2</td>
<td>3.3–9.2</td>
<td>–</td>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>SPME-GC/FID</td>
<td>Charcoal/PVC</td>
<td>Fruit juice</td>
<td>0.008–0.040</td>
<td>0.052–5.0</td>
<td>62</td>
<td>46</td>
<td>4.50–18.2</td>
<td>15</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>SPME-GC/NS</td>
<td>Polycarbonate</td>
<td>Juice/Wine</td>
<td>2–90</td>
<td>10–500</td>
<td>5–98</td>
<td>–</td>
<td>–</td>
<td>30</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>HS-SPME-GC/FID</td>
<td>PMDS</td>
<td>Fruit juice</td>
<td>0.025–0.050</td>
<td>74–117</td>
<td>&lt;20</td>
<td>45</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>MSPE-</td>
<td>3D-G-Fe₃O₄</td>
<td>Fruit juice</td>
<td>0.001–0.005</td>
<td>0.03–50</td>
<td>86.6</td>
<td>107.5</td>
<td>2.6–5.1</td>
<td>2</td>
<td>10</td>
<td>469–510</td>
</tr>
</tbody>
</table>

* Recovery.
* Extraction time.
* Preconcentration factor.
* Multi-walled carbon nanotube.
* (mg kg⁻¹).
* Cetyltrimethyl ammonium bromide.
* Flame thermionic detection.

3.2.5. Effect of salt concentration
Salt addition to aqueous samples can influence the extraction recovery. In this study, the effect of salt concentration was studied by adding different amounts of NaCl in the range of 0–20% (w/v) into the sample solution. As illustrated from the results in Fig. 3e, salt concentration of up to 10% (w/v) did not have a significant effect on the extraction recovery of OPPs. When the amount of NaCl was further increased, extraction recoveries decreased. The decrease in extraction recoveries can be due to increase in viscosity of sample solution which results in reduction of analyte mass transfer to the adsorbent surface. Considering these results and simplicity of extraction process, further experiments were carried out without salt addition.

3.3. Comparison of extraction recovery of 3D-G-Fe₃O₄ with 2D-G-Fe₃O₄ and Fe₃O₄
To investigate the performance of 3D-G-Fe₃O₄, its extraction recoveries for the OPPs were compared with those of both 2D-G-Fe₃O₄ and Fe₃O₄. The results in Fig. 4 indicated the extraction recoveries of 3D-G-Fe₃O₄ were higher than those obtained by 2D-G-Fe₃O₄ and Fe₃O₄ for all of the OPPs under similar conditions. This could be attributed to the very high specific surface area and three-dimensional nanoporous structure of 3D-G-Fe₃O₄. Based on the above results, 3D-G-Fe₃O₄ was an excellent choice as a promising adsorbent in the MSPE of the selected OPPs.

3.4. Reusability
Reusability of the adsorbent was investigated by evaluating extraction performance of 3D-G-Fe₃O₄ after it was subjected to
different extraction-desorption cycles. For this purpose, in each run, 50 mL of sample solution containing 50 ng L\(^{-1}\) of OPPs was extracted with 3D-G-Fe\(_3\)O\(_4\) according to the described procedure under optimal conditions. Any time, after completing each extraction procedure, the adsorbent was washed twice with acetone and distilled water respectively, and then the dried adsorbent was used in the next analysis run. Extraction recoveries were determined after each five cycle to save time and cost. The results showed that 3D-G-Fe\(_3\)O\(_4\) could be reused at least 35 times without a significant loss in extraction recoveries (<5%) and its magnetism property. These results suggest that the 3D-G adsorbent is enough stable for repeated uses which is favorable for SPE based methods.

Repeatability of the results for different synthesized batches of adsorbent is another important factor. In order to evaluate the repeatability of extraction performance, three batches of the adsorbent were synthesized and tested according to the proposed procedure (Section 2.4). Five replicated analyses were performed for each adsorbent (at the concentration level of 50 ng L\(^{-1}\) of each OPP and the mean extraction recoveries of OPPs and their variances were calculated. The experiments exhibited that the RSDs of mean extraction recoveries were between 1.5 and 3.4%. A student’s t-test was also applied with a confidence level of 95% (p = 0.05). The obtained data (Table S1 of the supplementary data) indicated that the extraction recoveries of two synthesized batches were not significantly different from each other. On the basis of obtained low RSDs (<3.4%) and student’s t-test results, the 3D-G-Fe\(_3\)O\(_4\) nanocomposite showed good reproducibility for the extraction of OPPs.

3.5. Analytical performance and real samples analysis

In order to validate the proposed method, a series of sample solutions containing the OPPs at seven concentration levels were prepared and analyzed under the optimal experimental conditions. For each concentration level, three replicate extractions and determinations were performed. Calibration curves were obtained by plotting peak areas versus concentrations of analytes. The results are given in Table 1. The limits of detection (LODs) and quantification (LOQs) of the method were obtained based on a signal-to-noise (S/N) ratio of 3 and 10, respectively. Good linearity was observed over the concentration range of 10–50000 ng L\(^{-1}\) for all of OPPs with satisfactory determination coefficients (r\(^2\)) from 0.9973 to 0.9999. Enhancement factors (EF) were defined as the ratio between final analyte concentration in organic solvent (100 μL acetone) and initial analyte concentration in sample solution (5000 ng L\(^{-1}\)).

The precision of the method was also studied at concentration level of 200 ng L\(^{-1}\) for each OPP. The intra-day precision was obtained by analyzing the samples five times in the same day, and the inter-day precision was obtained by performing the same process (five replicate) in three consecutive days. All the intra- and inter-day RSDs were lower than 6.9 for the OPPs.

In order to evaluate applicability of the proposed method, five kinds of fruit juices were selected and analyzed for detection of the OPPs. The fruit juices were purchased from a local supermarket. The samples were filtered through a 0.45 μm membrane filter and 50 mL of each was used for the MSPE procedure. The results are shown in Table 2. Trace amounts of phorate (18.7 ng L\(^{-1}\)), parathion-methyl (54.3 ng L\(^{-1}\)), fenitrothion (36.5 ng L\(^{-1}\)) and azinphos-methyl (20.1 ng L\(^{-1}\)) were found in the apple juice and no target analytes were detectable in the other samples. The observed concentrations were completely below MRLs fixed by the European legislation (Council Directives 90/642/EEC, 1990), which demonstrated that the OPPs residues in the apple juice were not serious. To determine the recoveries of the method, the fruit juice samples were spiked with the OPPs standards at two concentration levels of 20 and 200 ng L\(^{-1}\), respectively. The recoveries for the OPPs in fruit juice samples are listed in Table 2. The results indicated that the recoveries were in the range from 86.6 to 107.5% with RSDs between 2.5% and 7.4%.

Matrix effects can seriously affect the chromatographic signals of the analytes by suppression or enhancement of the signals due to probable co-extracting matrix substances. So, the matrix effect (ME) was investigated by analyzing all fruit juices under the optimized experimental conditions and calculated by the following equation (Eq. (2)):

\[ \text{Matrix effect} = \left( \frac{P_s - P_n}{P_w} \right) \times 100 \] (2)

where \(P_s\) is the peak area of the analyte in fruit juice sample spiked with 200 ng L\(^{-1}\) of OPPs standard solution, \(P_n\) is the peak area of the analyte in the non-spiked fruit juice sample and \(P_w\) is the peak area of the analyte in water spiked with 200 ng L\(^{-1}\) of OPPs standard solution. As can be seen from the results in Table 2, the matrix effect values were in the range of 83.4–103.2% for all of the OPPs in the fruit juice samples (three replicate analysis were performed and the mean values with RSDs were presented). Considering an acceptable interval for matrix effect is ranging from 70% to 120% according to the guidance document on analytical quality control and validation procedures for pesticide residues analysis in food and feed (SANTE/11945/2015), all investigated analytes meet these criteria. This indicated that the matrix of fruit juices did not have a significant effect on the performance of 3D-G-Fe\(_3\)O\(_4\) nanocomposite for OPPs extraction and therefore, use of matrix-matched calibration standards is not required. It should be stressed that a great selectivity was obtained using different fruit matrices because of non-significant matrix effect. The OPPs can attach to the adsorbent by strong \(\pi-\pi\) stacking interactions. The typical chromatogram of apple juice sample was shown in Fig. 5 before and after being spiked with each OPP at 20 and 200 ng L\(^{-1}\). A GC–MS analysis was also performed for the non-spiked fruit juices to confirm the GC-NPD results by retention time and EI spectra matching with standards. The GC–MS chromatogram of apple juice was presented in Fig. 6.

3.6. Comparison with other extraction methods

The performance of the developed MSPE-GC–MS method based on 3D-G-Fe\(_3\)O\(_4\) as adsorbent was compared with other reported SPE-based methods in the literature for the determination of OPPs [46–55]. As can be seen from Table 3, the proposed method showed comparable linearity, good precision and adequately low detection limits. Furthermore, the introduced method used lower amounts of adsorbent as a result of high adsorption capacity of porous structure of adsorbent. In addition, the method showed a very short extraction time because of the effective interaction between the analytes and the adsorbent. Compared with the traditional SPE methods [51,52], the magnetic adsorbent can be directly dispersed in the sample solution which avoids the time-consuming column passing or cartridge blocking. This makes separation process easier and faster without a need for additional centrifugation or filtration procedures. In addition, 3D-G-Fe\(_3\)O\(_4\) can be fabricated in large scales through a simple procedure with low cost of raw materials and could be reused several times without significant decrease in extraction efficiency. The results demonstrated the proposed method is simple, rapid, sensitive and efficient, and can be applied for routine monitoring of OPPs residues in fruit juices.

4. Conclusions

In this work, a 3D-G-Fe\(_3\)O\(_4\) nanocomposite was successfully synthesized by a simple self-assembly of reduced GO nanosheets decorated with Fe\(_3\)O\(_4\) nanoparticles. Owing to its high surface area, 3D nanoporous structure and excellent magnetic properties, the 3D-G-Fe\(_3\)O\(_4\) was used as a superior MSPE adsorbent for
Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chroma.2016.03.046.

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