Development of graphene-carbon nanotube-coated magnetic nanocomposite as an efficient sorbent for HPLC determination of organophosphorus pesticides in environmental water samples

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ABSTRACT
A magnetic solid-phase extraction (MSPE) method coupled to high performance liquid chromatography with UV (HPLC-UV) was proposed for the determination of organophosphorus pesticides (OPPs) at trace levels in environmental water samples. The ternary nanocomposite of graphene-carbon nanotube-Fe₃O₄ (G-CNT-Fe₃O₄) has been synthesised via a simple solvothermal process and the resultant material was characterised by powder X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) spectroscopy. Significant factors that affect the extraction efficiency, such as amount of magnetic nanocomposite, extraction time, ionic strength, solution pH and desorption conditions were carefully investigated. The results demonstrated that the proposed method had a wide dynamic linear range (0.005–200 ng mL⁻¹), good linearity ($R^2 = 0.9955–0.9996$) and low detection limits (1.4–11 pg mL⁻¹). High enrichment factors were achieved ranging from 930 to 1510. The results show that the developed method is suitable for trace level monitoring of OPPs in environmental water samples.

1. Introduction
Sample preparation methods generally involve a solvent or solid-phase-based extraction technique. The objective of sample preparation is to transfer the analyte from the sample matrix into a form that is pre-purified, concentrated and compatible with the analytical system [1]. Because of high enrichment factor, high recovery, low cost and low consumption of organic solvents, solid-phase extraction (SPE) has been become the most common technique for pre-concentration of analytes in various samples [2]. However, traditional SPE techniques require passing samples completely through cartridges filled with sorbents, followed by eluting the analytes with organic solvents. This method is tedious, time consuming and labour intensive, especially for large volumes of samples.

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To overcome these weaknesses, a new SPE technique was developed based on the combination of magnetic inorganic material and non-magnetic adsorbent, which is called magnetic solid-phase extraction (MSPE) [3]. The most important component of the MSPE technique is the adsorbent material, which dominates the selectivity and sensitivity of the method [4]. In recent years, carbonaceous materials have been received great attentions for adsorption applications because of their good chemical stability, structural diversity, low density and suitability for large scale [5,6,7,8]. Among the carbonaceous materials, carbon nanotubes (CNT) and graphene are considered as the most widely used materials because of their typical characteristics, such as high surface-area-to-weight ratio, good physical and chemical stability and low cost. Toward this end, the development of novel carbon-based materials to meet the practical application requirements is considered to be an important focus in the adsorption process [5].

Graphene, an emerging carbon material, has attracted tremendous attention due to its unique two-dimensional structure and superior properties [9]. The intrinsic van der Waals interactions between layers of graphene easily results in irreversible agglomeration or even restocked to form graphite. This limitation can be overcome by the attachment of other molecules or polymers onto the graphene surfaces [10]. Recently, the combination of 1D CNT with 2D graphene to give a 3D G-CNT hybrid nanocomposite has been reported [11], which exhibits the merits of both G and CNT. The CNT possesses one-dimensional structure and also exhibits high performance in the adsorption of organic chemicals [9]. Presence of CNT in the G nanocomposite can expand the layer distance between G sheets, and avoid the self-aggregation of graphene [11]. Therefore, this novel structure can provide maximum exposed carbon surfaces for the adsorption of analytes and increase the effective surface area, which can increased adsorption capacity [12]. Up to now, G and CNT are used separately with magnetic materials and were used in MSPE technique [13,14]. However, to the best of our knowledge, there are few investigations focused on the synthesis and adsorption properties of the magnetic G-CNT, which can combine the separation convenience of the magnetic materials and high adsorption capacity of G-CNT [15].

Organophosphorus pesticides (OPPs) are one of the most dangerous environmental pollutants because of their stability, mobility and long-term effects on living organisms [16,17]. Also many studies have proved mutagenic, carcinogenic [18], cytotoxic [19] and teratogenic [16] effects of OPPs. For environmental and drinking water, the maximum admissible concentration of a single compound established by the European Union is 0.1 µg L\(^{-1}\), and 0.5 µg L\(^{-1}\) is the maximum allowed limit for the total concentration of all pesticides [20]. Therefore, the development of a simple, rapid and sensitive analytical methods for monitoring of OPPs pollutants in environmental samples is required [17,21].

In this article, we report magnetic G-CNT as a highly efficient adsorbent with excellent separation properties for OPPs in water samples. Due to the unique morphological properties of the G-CNT, the adsorption behaviour of G-CNT-Fe\(_3\)O\(_4\) is more improved in comparison with Fe\(_3\)O\(_4\), G-Fe\(_3\)O\(_4\) and CNT-Fe\(_3\)O\(_4\). After optimisation of the extraction conditions, the established method was applied to real water samples. This method shows an excellent adsorption capacity, low limit of detection (LOD) and high enrichment factor for detection of OPPs.
2. Experimental

2.1. Chemicals and water samples

Pesticide analytical standards include malathion (Mala), diazinon (Diaz), phosalone (Phos) and chlorpyrifos (Chlor) were provided by Fluka (Germany) (Table 1 shows their structures and IUPAC names). All pesticide standards were about 97.7–99.5% purity. Standard solutions of each compound at a concentration of 100 µg mL⁻¹ were prepared in methanol and stored at 25°C. Methanol liquid chromatography (LC)-grade was used for standard preparation and chromatographic analysis. Multi-wall CNTs, graphite powder, ferric chloride hexahydrate (FeCl₃·6H₂O), sodium acetate (NaAc) and ethylene glycol (EG) sodium hydroxide and hydrochloric acid were used for pH adjustment and sodium chloride was used for ionic strength studies. All chemicals are from Merck (Darmstadt, Germany).

2.2. Instrumentation

A Jasco HPLC system, consisted of an isocratic pump (JASCO-1580), a Rheodyne 7725i injector with a 20-µL loop (Rheodyne, Cotati, CA, USA) and a spectrophotometric detector (JASCO-1575) were used in the experiment. The chromatographic system was controlled by HSS-2000 provided by Jasco using the LC-Net II/ADC interface. The data

Table 1. Name, abbreviation and chemical structures of the target analytes.

| Name | Abbreviation | Chemical structure |
|------|--------------|--------------------|
| Malathion: Diethyl 2-[[(dimethoxyphosphorothioyl)sulfanyl]butanedioate | Mala | ![Chemical structure of Mala](image) |
| Diazinon: O,O-Diethyl O-[4-methyl-6-(propan-2-yl)pyrimidin-2-yl]phosphorothioate | Diaz | ![Chemical structure of Diaz](image) |
| Phosalone: 6-chloro-3-(diethoxyphosphinothioylsulfanylmethyl)-1,3-benzoxazol-2-one | Phos | ![Chemical structure of Phos](image) |
| Chlorpyrifos: O,O-Diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate | Chlor | ![Chemical structure of Chlor](image) |
were processed using BORWIN software (version 1.50). An analytical column Perfectsil target ODS-3 (250 mm × 4.6 mm ID, 5-μm) (MZ-Analysentechnik, Germany) with an ODS-3 precolumn (10 mm × 4.0 mm I.D., 5 μm), which was maintained at ambient temperature was employed for separation.

In order to identify the crystal structure of as-prepared nanoparticles (NPs), powder X-ray 124 diffraction (XRD) measurements were performed by employing a Bruker D8 Advance (Bruker AXS, Karlsruhe, Germany) instrument with Cu-Kα radiation source (1.54 Å) between 6 and 70° generated at 40 kV and 35 mA at room temperature. In addition, Fourier transform infrared (FTIR) spectra (4000–400 cm⁻¹) were recorded on a Vector 22 (Bruker, Ettlingen, Germany) FTIR spectrometer using the KBr pellet with a ratio sample/KBr of 1:100 by mass. The morphology of G-CNT-Fe₃O₄ were characterised by scanning electron microscope (SEM) model LEO1430 vp (LEO Electron Microscopy Inc., Carl Zeiss, Germany) and transmission electron microscope (TEM) model 906 E (Zeiss, Göttingen, Germany).

2.3. Preparation of G-CNT-Fe₃O₄ nanocomposite

Graphite oxide (GO) was synthesised according to the modified Hummers’ method [22]. CNT were pre-treated by blending the CNT (0.5 g) with 60 mL of sulphuric acid and nitric acid mixture (mole ratio: 3/1). This solution was dispersed by ultrasonication for about 2 h and refluxed under magnetic stirring at 80°C for 6 h. Then, the dispersed solution was filtered and the particles obtained were washed to neutrality, and dried in vacuum at 65°C overnight. A solvothermal method was carried out to prepare magnetic nanocomposites. To prepare magnetic G-CNT nanocomposite, first 400 mg of GO and 80 mg CNT were added in 80 mL of EG and then ultrasonically (138 W, 59 kHz) exfoliated for 2 h to achieve a uniform mixed solution. Then, 2.5 g FeCl₃·6H₂O and 3.8 g NaAc were added into the GO-CNT solution under stirring. Subsequently, the mixture was put into an autoclave and heated at 200°C for 6 h and then cooled to room temperature. The product was washed three times with water and three times with ethanol, then dried at 40°C under vacuum. To maximise the pre-concentration property of G-CNT-Fe₃O₄ nanocomposites, various ratios of GO/CNT (1:5, 1:2, 1:1, 2:1 and 5:1) were utilised and optimised.

2.4. Magnetic solid-phase extraction procedures

First of all, 80 mg of adsorbent (G-CNT-Fe₃O₄ nanocomposite) was rinsed in 5 mL methanol and 5 mL deionised water and then dispersed into an 800 mL aqueous sample solution by ultrasonication (15 min) (60 W, 40 kHz) to form a homogeneous suspension and finally stirred in a vortex (1 min) to favour the extraction of the target analytes. After that, the G-CNT-Fe₃O₄ was separated from the aqueous phase by placing an Nd-Fe-B strong magnet at the bottom of the beaker. After about 5 min, the suspension became limpid and the liquid was decanted. The pre-concentrated target analytes were eluted from the adsorbent with 8 mL of acetonitrile with the aid of ultrasonication for 5 min. To maximise the detection sensitivity, desorption solution was evaporated to dryness under a mild stream of nitrogen at 25°C and its volume was adjusted to 0.5 mL. A 20 µL of this solution was injected into the HPLC system for
Prior to next use, the used G-CNT-Fe$_3$O$_4$ was first washed three times each with 1 mL acetonitrile and then with 1 mL acetone by vortexing for 2 min, respectively.

### 2.5. Sample preparation

The recovery studies were carried out using tap water, well water, river water and mineral water samples. Tap water sample was collected freshly from our laboratory (Azarbaijan University of Shahid Madani, Tabriz, Iran) and well water came from deep ground water in Tabriz (Iran). River water (Sufi Chay River, Maragheh, Iran) was picked up a few days before analysis. The mineral water sample was collected from Kandovan (East Azarbaijan Province, Iran). All the environmental water samples were collected in brown bottles and were filtered through 0.45 mm microporous membranes immediately after sampling, and stored in the dark place at 4°C until analysis. Initial analysis confirmed that they were free of target analytes.

### 2.6. Chromatographic conditions

The isocratic mobile phase consisted of methanol-phosphate buffer (25 mM) (pH = 5) in the ratio of 80:20 v/v, flowing through the column at a constant flow rate of 1 mL min$^{-1}$ [23]. The eluent was monitored using UV detection at a wavelength of 225 nm. The mobile phase was filtered through a 0.22 mm membrane-type GV filter (Millipore). A 40 kHz and 138 W ultrasonic water bath with temperature control (sonic bath model LBS2–FALC instruments S.r.ITREVI GLIO, Italy) was applied to degassing the mobile phase. The chromatographic peak areas were used for providing calibration curves and estimation of the extraction efficiency under various experimental conditions.

### 3. Results and discussion

#### 3.1. Characterisation of magnetic G-CNT nanocomposite

XRD measurements were performed to obtain crystalline structural information for the as-synthesised Fe$_3$O$_4$, graphene oxide (GO), G-CNT and G-CNT-Fe$_3$O$_4$ (Figure 1(a)). The diffraction peak of GO was observed at about $2\theta = 10.6^\circ$, which corresponds to the (001) reflection of graphene oxide. The results are in good agreement with the reported works about GO [24]. According to reports, the pure CNT exhibit a sharp peak at 26.06° of (002) plane [25,26], while the graphene displays a very broad peak at about 26° [27]. As for the G-CNT nanocomposite, the peak at ca. 26° is relatively strong and broad, which was a result of the overlap by CNT and graphene. This fact solidly confirmed that GO was successfully reduced to graphene nanosheets [9]. The XRD pattern of G-CNT-Fe$_3$O$_4$ shows a broad peak corresponding to the (002) reflection of graphene and CNT at 26°, suggesting that the samples are poorly ordered along the stacking direction. This is an indication that the sample comprises largely free G sheets. Except the diffraction peak at $2\theta = 26^\circ$ resulting from G-CNT, all the other significant diffraction peaks of the G-CNT-Fe$_3$O$_4$ sample matched well with data from the Joint Committee on Powder Diffraction Standards card (19-0629) for Fe$_3$O$_4$ (the diffraction angles at 2): 30.2°, 35.6°, 43.3°, 53.7°,
57.3° and 62.8°, which can be assigned to (220), (311), (400), (422), (511) and (440) of crystal planes of Fe$_3$O$_4$.

FTIR spectra of GO, G-CNT, Fe$_3$O$_4$ and G-CNT-Fe$_3$O$_4$ nanocomposite are shown in Figure 1(b). In the FTIR spectrum of the GO, the absorption peak at 3424 cm$^{-1}$ showed the O–H stretching band. The peaks at 1700 and 1377 cm$^{-1}$ were the C=O stretching vibration peaks of carboxyl and carbonyl; the peak at 1628 cm$^{-1}$ was attributed to the stretching vibration of aromatic C=C; the peaks at 1230 and 1059 cm$^{-1}$ were ascribed to the C–O stretching vibration of epoxy group and alkoxy [29]. These peaks demonstrate the existence of carboxyl, epoxy group and alkoxy in graphene oxide. The overall spectral pattern and number of bands for the GO and G-CNT nanocomposite were almost similar, except for their intensity. In comparison with GO, G-CNT nanocomposite

Figure 1. (a) X-ray diffraction (XRD) patterns and (b) FTIR spectra of GO, G-CNT, G-CNT-Fe$_3$O$_4$ and Fe$_3$O$_4$. 
showed a dramatic decrease in the intensity of the adsorption peaks of oxygen-containing functional groups, which suggested that graphene oxide has been partially reduced. The characteristic absorption peaks of G-CNT also coexisted in the spectrum of the G-CNT-Fe$_3$O$_4$ nanocomposite, which confirmed the existence of graphene sheets and CNT in the nanocomposite. The broad absorptions at low frequencies are ascribed to the vibration of Fe–O bond (570 cm$^{-1}$), which was not observed in the spectrum of G-CNT [28]. This peak proved that Fe$_3$O$_4$ NPs was successfully anchored onto G-CNT nanocomposite. Moreover, the intensity of peaks in G-CNT-Fe$_3$O$_4$ nanocomposite is larger than that of the G-CNT, which represents indirectly that Fe$_3$O$_4$ NPs are grown on surface of G-CNT with the aid of the oxygen functionalities as reactive sites at the graphene surface and thus ensuring the strong interfacial interaction and structural stability of G-Fe$_3$O$_4$ nanocomposite [30].

Morphology and structure of the synthesised G-CNT-Fe$_3$O$_4$ nanocomposite were investigated by SEM and TEM in Figure 2. The representative SEM images of

![Figure 2](image_url). Typical SEM (a, b) and TEM (c, d) images of G-CNT-Fe$_3$O$_4$ nanocomposite.
magnetic G-CNT nanocomposite (Figure 2(a) and (b)) demonstrated a considerably rough surface with magnetite beads on the surface of graphene sheets and CNT, which suggested the successful combination of Fe3O4 onto the surface of graphene and CNT. Furthermore, the TEM images of magnetic G-CNT nanocomposite (Figure 2(c) and (d)) indicated that graphene had a nearly transparent flake-like shape with characteristic single-layer nature. The flexible CNT intricately grew on the basal planes of graphene, where a rough surface was covered with the anisotropic assembled CNT, confirming that the incorporation of the one-dimensional CNT into two-dimensional graphene formed a hierarchical structure. Based on these observations, it is expected that the G-CNT-Fe3O4 nanocomposite shows higher adsorption capacity compared to the both CNT-Fe3O4 and G-Fe3O4 nanocomposites. Many Fe3O4 particles with a size of 120–200 nm were homogeneously anchored onto the surface of graphene and CNT to form a G-CNT-Fe3O4 nanocomposite.

The GO to CNT ratio was an important factor in the stability and extraction efficiency of the synthesised adsorbent, which was optimised using various amounts of them. To find the optimum ratio of the nanocomposite, G-CNT-Fe3O4 nanocomposite with different ratio of GO to CNT (5:1, 2:1, 1:1, 1:2, 1:5) was prepared and the extraction efficiency of resulting G-CNT-Fe3O4 nanocomposite for the OPPs was comparatively studied (Figure 1S). It was observed that the ratio of 5:1 (GO:CNT), represented the highest extraction rate and stability. Therefore, this ratio was taken as the optimum ratio of GO to CNT.

3.2. Optimisation of the MSPE conditions

In order to achieve a satisfactory extraction performance of the proposed MSPE based on magnetic G-CNT procedure for the four OPPs, several parameters, including amounts of G-CNT-Fe3O4 nanocomposite, type and volume of elution solvent, adsorption time, elution time, ionic strength, solution pH and solution volume were examined and optimised. Ultrapure water samples spiked with 30 ng mL\(^{-1}\) of Mal and Diaz, 15 ng mL\(^{-1}\) of Phos and Chlor were used for these optimisation experiments. And all the experiments were performed in triplicate and the means of the results were used for optimisation. Analytes in aqueous matrices were extracted, concentrated and injected into the high performance liquid chromatography with UV (HPLC-UV) for analysis. The chromatographic peak area, which is proportional to analyte concentration, was used to construct calibration curves and estimate the extraction efficiency under different experimental conditions.

3.2.1. Extraction efficiency of Fe3O4, G-Fe3O4, CNT-Fe3O4 and G-CNT-Fe3O4 adsorbents

Figure 3 shows comparatively the capabilities of Fe3O4, G-Fe3O4, CNT-Fe3O4 and G-CNT-Fe3O4 nanocomposites for the extraction of four OPPs from the 500 mL sample volume. The experimental results indicated that both CNT-Fe3O4 and G-Fe3O4 could extract the compounds from the sample solution, but the Fe3O4 NPs alone could not, suggesting that CNT or G was responsible for the adsorption of the OPPs on the sorbents. This can be attributed to the presence of carboxyl and hydroxyl groups on
the surface of CNT-Fe$_3$O$_4$ and G-Fe$_3$O$_4$ in comparison with Fe$_3$O$_4$ magnetic nanoparticles that make them completely suitable for effective interaction with analytes and adsorb them. It can be also seen that the binary adsorbents, G-CNT, exhibit enhanced adsorption performance than single ones alone (i.e. G and CNT). The G-CNT-Fe$_3$O$_4$ can combine the separation convenience of the magnetic materials and higher adsorption capacity of G-CNT. Based on the experimental results, the G-CNT-Fe$_3$O$_4$ was selected for the extraction of the four OPPs.

3.2.2. Influence of G-CNT-Fe$_3$O$_4$ amount
In order to select an optimum amount of the G-CNT-Fe$_3$O$_4$ for extraction of the analytes, different dosages of the G-CNT-Fe$_3$O$_4$ were investigated in the range from 10 to 120 mg. The results shown in Figure 4 revealed that the peak areas for the analytes were increasing rapidly when the amount of the G-CNT-Fe$_3$O$_4$ was increased from 10 to 80.0 mg and then remained almost unchanged. Therefore, 80 mg G-CNT-Fe$_3$O$_4$ was selected for the following experiments.

3.2.3. Effect of extraction time
In MSPE process, the extraction time is one of the main factors that influence the extraction efficiency. The effect of extraction time on the extraction efficiency was investigated in a range of 2–30 min and the results are shown in Figure 5. It can be seen that the peak areas are enhanced by increasing the extraction time up to 15 min. After 15 min, the extraction efficiency remained nearly constant. Therefore, the extraction time of 15 min was selected.
3.2.4. Desorption conditions

Desorption of the analytes from the magnetic nanocomposite is a crucial part in the whole process. In this work, organic solvents, the amount of eluent and desorption time used for MSPE procedure were optimised. Figure 6(a) shows the desorption efficiency of OPPs using different types of desorption solvents, including methanol, acetonitrile, acetone and hexane. As a result, under the same extraction and elution conditions,
Figure 6. Effect of different eluting solvent (a), eluent volume (b) and desorption time (c) on extraction of OPPs. The amount of G-CNT-Fe$_3$O$_4$ was 80 mg and extraction time, 15 min. Other extraction conditions are as indicated in Figure 3.
acetonitrile provided the best desorption efficiency and the OPPs could be desorbed quantitatively from the adsorbent. Thus, acetonitrile was chosen as the desorption solvent.

To optimise the eluting volume, different volumes (2, 4, 8 and 10 mL) of an elution solvent (acetonitrile) were used as shown in Figure 6(b). It was found that 8 mL desorption solvent could completely elute the extracted OPPs from the G-CNT-Fe₃O₄. Thus, 8 mL was selected as optimum elution volume for this method.

Meanwhile, the effect of desorption time was studied. The peak area after desorption for 2, 5, 10 and 20 min were unchanged, suggesting that desorption time had no obvious influence on the desorption efficiency. Therefore, desorption time of 5 min was selected.

3.2.5. Influence of sample solution pH and salinity

In adsorption process, sample solution pH is an important factor since it could influence the physicochemical properties of both the adsorbent and the adsorbate [13]. Taking into account the instability of OPPs under strong acidic and alkaliescent condition [31], the pH was investigated in the range of 4–8 (data not shown). The results showed that the extraction recoveries for the OPPs were almost unchanged when the pH was changed from 4 to 8. This could be because the OPPs exist as neutral molecules under ordinary conditions and are relatively unsusceptible to the changes of sample solution pH. Therefore, no particular pH adjustment was performed during the remaining of the work.

Adding the salt in an aqueous solution had two influences in extraction efficiency, salting-in and salting-out effects. Solubility of some analytes in the aqueous phase were increased by salting-in effect due to increase in the ionic strength of solution. This effect decrease extraction efficiency of analytes [13]. Salting-out effect is based on the electrolyte–nonelectrolyte interaction, making less solubility of non-electrolyte (analytes). In this condition, the extraction efficiency to organic solvent could be enhanced. The presence of salt can be changed by the extraction efficiency, depending on the nature of analytes, the type of adsorbent and salt concentration [32,33]. Hence, the effect of salt concentration was studied by adding different amounts of NaCl (0–15% w/v) into the sample solution. As shown in Figure 7, the highest peak area was observed when there is no salt added. The extraction efficiency decreased with further increasing the concentration of NaCl. The decrease can be explained by salt-in effect, preventing the target analytes to extract by G-CNT-Fe₃O₄ [34]. Considering the extraction efficiency and simplicity of the extraction process, further experiments was performed without the addition of salt.

3.2.6. Reusability of the adsorbent

The reusability of the G-CNT-Fe₃O₄ adsorbent was investigated in this study. After each use of the magnetic adsorbent, it was washed three times each with 1 mL acetonitrile and then with 1 mL acetone by vortexing for 2 min, respectively. After washing, no sample carryover was detected and the adsorbent was ready for the next use. It was found that the recoveries of the OPPs are not diminished even after 15 successive extraction processes, suggesting the good reusability of the adsorbent.
3.2.7. Effect of sample volume

To achieve better extraction efficiency and higher enrichment factor with shorter operational time, the effect of the sample volume was studied by using a series of different volume of sample solutions (100–1000 mL) with the fixed amount of all analytes and the adsorbent. The recovery was found to be stable when the sample volume was in the range of 100–800 mL, and then slightly decreased with further increase of sample volume. Thus, 800 mL was considered to be the optimal sample volume. By extracting analytes from 800 mL aqueous solution and after drying the eluent with a nitrogen stream at 25°C and re-dissolving in 0.5 mL acetonitrile, the enrichment factors achieved for Mala, Diaz, Phos, and Chlor are 930, 1158, 1450 and 1510, respectively.

3.3. Method evaluation and real sample analysis

3.3.1. Validation of the HPLC coupled with the proposed MSPE method

The figures of merit of the calibration curves, LODs, estimation coefficients ($R^2$) and the repeatability were performed under the conditions optimised above for the OPPs based on external standard calibration. In the construction of the calibration curve, triplicate measurements of each concentration level of the calibration samples were performed and the calibration curves were obtained by plotting peak area versus concentrations. Experimental calibration curve consists of two segments with different slopes. The sensitivity of the method was established by examining the LODs and limits of quantitation (LOQs). LOD and LOQ are defined as the lowest detectable and quantifiable concentration with a signal-to-noise ratio of 3 and 10, respectively. The values of LOD and LOQ were calculated based on calibration equation obtained for lower concentrations of analytes. All analytes exhibited good linearity with satisfactory regression coefficients ($R^2 = 0.9955–0.9996$). According to the experimental
results (Table 2), the LODs and LOQs data were in the range of 1.4–11 and 4.5–35 pg mL\(^{-1}\), respectively.

### 3.3.2. Analysis of environmental water samples

The MSPE-HPLC method developed in this work was used to analyse several environmental water samples, including tap water, well water, river water and mineral water. Initial analysis confirmed that they were free of target analytes. To estimate the influence of the matrix, all of the samples were spiked with the analytes at two concentrations levels (10 and 20 ng mL\(^{-1}\) for both Mala and Diaz, 2 and 4 ng mL\(^{-1}\) for both Phos and Chlor) to determine the recovery of the targeted analytes. Recoveries (R\%) for the analysis of OPPs in spiked water samples using the proposed method based on three replicate extractions and determinations are shown on Table 3. The results indicated that the recoveries of spiked water samples are very satisfactory. The recoveries for the four OPPs were in the range from 75.6–102.5\% with relative standard deviations (RSDs) between 3.2\% and 8.4\%. Thus, the method was suitable for analysing the water samples.

The typical chromatograms recorded for Sufi Chay River water sample before (a) and after (b) spiked with Mala and Diaz (10.0 ng mL\(^{-1}\)) and Phos and Chlor (2 ng mL\(^{-1}\)) were shown in Figure 8.

### Table 2. The analytical performance data obtained for target analytes.

| Compound | Linear range (ng mL\(^{-1}\)) | LOD\(^a\) (pg mL\(^{-1}\)) | LOQ\(^b\) (pg mL\(^{-1}\)) | RSD (%) (n = 3) |
|----------|-----------------|----------------|----------------|-----------------|
| Mala     | 0.1–1           | 10             | 28             | 6.5             |
|          | 1–200           |                |                |                 |
| Diaz     | 0.1–2           | 11             | 35             | 4.6             |
|          | 2–100           |                |                |                 |
| Phos     | 0.01–0.5        | 2.6            | 8              | 3.9             |
|          | 0.5–25          |                |                |                 |
| Chlор    | 0.005–0.15      | 1.4            | 4.5            | 8.8             |
|          | 0.15–50         |                |                |                 |

Notes: \(^a\) Limits of detection (S/N = 3).  
\(^b\) Limits of quantification (S/N = 10).

### Table 3. Recoveries obtained in the determination of OPPs in spiked water samples.

| Analyte | Spiked (ng mL\(^{-1}\)) | Tap water (n = 3) | Well water (n = 3) | River water (n = 3) | Mineral water (n = 3) |
|---------|-------------------------|------------------|-------------------|---------------------|-----------------------|
|         | measured (ng mL\(^{-1}\)) | R\(^2\) + RSD (%) | measured (ng mL\(^{-1}\)) | R\(^2\) + RSD (%) | measured (ng mL\(^{-1}\)) | R\(^2\) + RSD (%) |
| Mala    | 0                       | ND\(^b\)         | 80 + 4.4          | 8.8 + 3.2           | 7.56 + 5.2            | 9.2 + 7 |
|         | 10                      | 18.5             | 92.5 + 6.7        | 8.2 + 4.9           | 17.9 + 8.6            | 19.1 + 9.5 + 4.2 |
| Diaz    | 0                       | ND\(^b\)         | 90 + 3.9          | 8.6 + 4.4           | 8.9 + 7.8             | 9.4 + 19 + 5.6 |
|         | 10                      | 17               | 85 + 6.6          | 8.1 + 4.1           | 17.4 + 87 + 7         | 19 + 95 + 7.5 |
| Phos    | 0                       | ND\(^b\)         | 95 + 7.2          | 1.8 + 5.2           | 1.84 + 92 + 6.7       | 1.9 + 95 + 8 |
|         | 2                       | 1.9              | 90 + 8            | 3.87 + 96.75        | 3.5 + 87.5 + 4.4      | 3.2 + 19 + 5.6 |
| Chlor   | 0                       | ND\(^b\)         | 95.5 + 5.1        | 2.05 + 102.5 + 7    | 1.91 + 97 + 5.9       | 1.85 + 92.5 + 6.7 |
|         | 2                       | 3.6              | 90 + 8            | 3.9 + 97.5 + 8.4    | 4.1 + 102.5 + 6.9     | 3.88 + 97 + 8.2 |
|         | 4                       | 3.8              | 95 + 4.8          | 3.9 + 97.5 + 8.4    | 4.1 + 102.5 + 6.9     | 3.88 + 97 + 8.2 |

Notes: \(^a\) R: recovery of the method.  
\(^b\) ND: not detected.
3.3.3. Comparison of MSPE with other methods
In order to further demonstrate the superiority of our proposed method, a comparison of the important features of the proposed method with those reported in the literature [1,5,20,23,31,33–41] is given in Table 4. As could be seen, the proposed method exhibited wider linear ranges, lower LODs and good reproducibility. The results revealed that the proposed method for the analysis of OPPs in water sample was simple, reliable and sensitive.

4. Conclusions
In this work, the magnetic graphene-carbon nanotubes-Fe$_3$O$_4$ (G-CNT-Fe$_3$O$_4$) nanocomposite was prepared by a solvothermal method and applied as an efficient adsorbent for

![Figure 8. The typical chromatograms recorded for Sufi Chay River water sample before (a) and after (b) spiked with Mala and Diaz (10.0 ng mL$^{-1}$) and Phos and Chlor (2 ng mL$^{-1}$).](image)

Table 4. Comparison of the current MSPE method with other sample preparation techniques for the determination of the OPPs.

| Methods                        | Linear range (ng mL$^{-1}$) | LOD (pg mL$^{-1}$) | EF | RSD (%) | Sample     | Reference |
|--------------------------------|------------------------------|--------------------|----|---------|------------|-----------|
| HF-MMILLE/LC-MS-MS$^c$         | 10–10,000                    | 3000–330,000       | 4.7–7.6 | Orange juice | [35]       |
| SPME/GC-NPD                    | 0.1–10                       | 6–120              | 7–17 | Water   | [36]       |
| MWCNT-SPE/HPLC-UV$^b$          | 1–500                        | 1–4                | 500  | 1.5–1.8 | Water      | [21]       |
| SPME/GC-FPD                    | 1–50                         | 10–300             | 3–9 | Water   | [35]       |
| IL-DLLME/HPLC-UV               | 10–1000                      | 100–5000           | >200 | 2.4–4.7 | Water      | [27]       |
| SDME/GC-MS                     | 0.5–100                      | 10–70              | 8.6–93 | Water   | [38]       |
| CPE-back extraction/GC-FPD     | 0.1–20                       | 40–80              | 3.4–4.7 | Urine   | [39]       |
| LPME/GC-MS$^c$                 | 0.1–100                      | 6–200              | 5–8 | Water   | [20]       |
| LSE/HPLC-DAD$^d$               | 0.4–5                        | 40–200             | 2–5 | Water   | [40]       |
| VSSLME/GC-FPD$^e$              | 0.1–50                       | 10–50              | 282–309 | 2.3–8.9 | Wine      | [41]       |
| MSPE/HPLC–UV                   | 0.05–400                     | 4–47               | 330–1200 | 3.7–6.6 | Water      | [1]        |
| MSPE/HPLC–UV                   | 0.005–200                    | 1.4–11             | 930–1530 | 3.9–8.8 | Water      | This work |

Notes: $^a$Hollow fibre microporous membrane liquid–liquid extraction.
$^b$Multi-walled carbon nanotube–solid phase extraction.
$^c$Liquid-phase microextraction.
$^d$On-line liquid–solid extraction.
$^e$Vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction.
the extraction of OPPs from environmental water samples prior to HPLC-UV detection. The study demonstrates that the proposed material is effective and efficient for sample preparation. G-CNT-Fe$_3$O$_4$ shows an excellent adsorption capacity, low LOD, high enrichment factor for the analytes due to carbon nanomaterials localised in the 3D porous structures. The developed method is efficient and easy to be used, without the need of additional centrifugation or filtration procedures. The G-CNT-Fe$_3$O$_4$ can be reused at least 15 times without a significant loss of the sorption capacity and magnetism. Applying G-CNT-Fe$_3$O$_4$ as adsorbent for the extraction of other organic pollutants from complex samples can be expected.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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