



Development of magnetic dispersive microsolid-phase extraction using lanthanum phosphate nanoparticles doped on magnetic graphene oxide as a highly selective adsorbent for pesticide residues analysis in water and fruit samples

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Abstract

Magnetic graphene oxide/lanthanum phosphate nanocomposite (MGO@LaP) was synthesized and used as an efficient adsorbent for magnetic dispersive microsolid-phase extraction (MD- μ -SPE) of pesticides before gas chromatography–electron capture detector (GC–ECD) analysis. The adsorbent was thoroughly characterized with scanning electron microscopy, vibrating sample magnetometer, energy-dispersive X-ray spectroscopy, and Fourier transform infrared spectroscopy. Optimized extraction conditions were investigated concerning extraction time, adsorbent amount, sample pH, and salt amount as well as desorption conditions (type and volume of desorption solvent and desorption time). Under the optimal conditions, the method demonstrated good linearity (3–1500 $\mu\text{g L}^{-1}$) with satisfactory determination coefficients of >0.997 and low detection limits for both chlorpyrifos (0.67 $\mu\text{g L}^{-1}$) and hexaconazole (0.89 $\mu\text{g L}^{-1}$). Finally, the method showed high analyte relative recoveries in the range of 78–120% for the determination of the selected pesticides in water and fruit juice samples.

Keywords Lanthanum phosphate · Graphene oxide · Magnetic dispersive microsolid-phase · Pesticides · Fruit juice · water sample

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Introduction

Pesticides are organic substances that are released deliberately into the environment for pest control; and thus can enhance the quantity and quality of fruits, vegetables, and crops all over the world. Despite their popularity and extensive use, pesticides are highly toxic, environmentally mobile, and stable compounds. Regarding the misuse of these compounds in agricultural products such as fruits, humans are exposed to unacceptable levels of pesticides. Some pesticides are known to cause different diseases such as cancer, asthma, hormone disruption, and allergies [1, 2]. Due to the adverse effects of pesticides on human health, the levels of their residues in food commodities are issues of global concern and are regulated by many legislations [3]. Hence, the European Union (EU) has established maximum residue limits (MRLs) for pesticide residues in fruits in the range of 10–50 $\mu\text{g L}^{-1}$ [4].

Several analytical techniques have been applied to determine pesticide residues in real samples. The typical techniques for analysis pesticides include gas chromatography (GC) [5], high-performance liquid chromatography (HPLC) [6]. GC, coupled with selective detectors, is commonly used for analyzing non-polar and volatile pesticide residues [7]. Before instrumental analysis of the pesticides, sample preparation is an essential step for efficient extraction, preconcentration, and purification of analytes, mainly when the analytes existed in trace levels [8]. In this regard, solid-phase extraction (SPE) has been considered as an effective method due to its compatibility with various matrices, flexibility, high enrichment factor, and low cost. Although SPE shows comprehensive advantages, it needs cartridge conditioning, washing, and elution with an organic solvent. Cartridge clogging, the high volume of sample loading, and low breakthrough volume are also SPE drawbacks. In order to overcome these problems, magnetic SPE (MSPE) is employed using magnetic adsorbents in batch mode for quick extraction of the analytes [9, 10]. Some potential benefits of MSPE are simplicity, time and labor saving, low solvent consumption, high precision, and satisfactory extraction efficiency. It should be considered that the type of MSPE adsorbents directly influences the adsorption selectivity and extraction efficiency of target analytes [11, 12].

Among the adsorbents used in MSPE, graphene oxide (GO) with large surface area and quantities of epoxy, hydroxyl, and carboxyl groups provide rich functional groups for the formation of hydrogen bonding, hydrophobicity, π - π stacking interactions with aromatic organic compounds containing oxygen and nitrogen functional groups [13]. However, the surface functionalization of GO with various molecules such as nanomaterials leads to improve the selectivity of the extraction system and achieve better adsorption properties [14]. The introduction of lanthanum phosphate nanoparticles (LaP NPs) with high chemical stability, low toxicity, and low water solubility to GO can combine the benefits of both materials [15]. Since LaP NPs form hydrogen bonding and electrostatic interactions toward organic compounds, it can be selected to provide targeted and enhanced adsorbent. In the present study, GO was doped with LaP on to enhance

the adsorption of pesticide residues from complex matrices. It was used as an efficient adsorbent for magnetic dispersive microsolid-phase extraction (MD- μ -SPE) of chlorpyrifos (CPS) and hexaconazole (HEX) as model compounds in fruit juices and tap water sample before gas chromatography–electron capture detector (GC–ECD) analysis. CPS and HEX were chosen due to the popularity of usage in developing countries for the protection of plants, especially in fruits and vegetables. Various interactions between the adsorbent and the selected pesticides, including hydrophobic, hydrogen bonding, electrostatic, and π – π interactions, indicated that the adsorbent was capable of extracting the analytes from sample solution efficiently. The experimental parameters affecting MD- μ -SPE conditions were investigated and optimized. Under the optimum conditions, the validation of MD- μ -SPE method was successfully carried out.

Experimental

Chemicals and reagents

The chemicals including acetonitrile (ACN), acetone, methanol (MeOH), *n*-hexane, toluene, hydrogen peroxide (H₂O₂, 30%), phosphoric acid, nitric acid (HNO₃), sulfuric acid (H₂SO₄, 98%), hydrochloric acid (HCl, 37%), ammonia, sodium hydroxide (NaOH), sodium chloride (NaCl), ammonium, ferrous sulfate [(NH₄)₂Fe(SO₄)₂·6H₂O] and iron (III) chloride hexahydrate (FeCl₃·6H₂O) were purchased from Merck Chemicals (Darmstadt, Germany). Lanthanum chloride (LaCl₃·6H₂O), CPS, and Hex were bought from Sigma-Aldrich (St. Louis, MO, USA). The standard working solution of CPS and HEX (1 mg L⁻¹) was prepared in MeOH and kept at 4 °C until use.

Instrumentation

The infrared spectra were recorded as KBr pellets on a PerkinElmer FT-IR RX1 (Waltham, MA, USA) in the range of 500–4000 cm⁻¹. The morphological characteristics and elemental compositions of the adsorbent were studied using field emission scanning microscopy–energy-dispersive X-ray spectroscopy (FE-SEM–EDX) (Tescan, MIRA-3, Czech Republic). The magnetic properties of the synthesized materials were investigated using a vibrating sample magnetometer (VSM/AGFM Meghnatis Daghigh Kavir Co., Kashan, Iran). X-ray diffraction (XRD) analysis of the adsorbent was studied by a Philips Analytical Diffractometer (X'Pert Pro system, MPD model, Almelo, Netherlands) with Cu K α radiation. The extracted pesticides were analyzed with an Agilent GC (7890A) equipped with an ECD detector and an HP-5ms capillary column (30 m × 0.25 mm × 0.25 μ m). The injector and detector temperatures were set at 280 and 300 °C, respectively. The injections were carried out in splitless mode (splitless time: 3 min). Helium (99.999%) was used as carrier gas at the flow rate of 1 mL min⁻¹, and nitrogen (99.999%) was used as detector make-up gas at a flow rate of 30 mL min⁻¹. The column temperature was

programmed as follows: the initial temperature 100 °C (held for 3 min), heated up at 35 °C min⁻¹ to 200 °C (fixed for 1 min), and finally raised at 25 °C min⁻¹ to 265 °C and held for 4 min.

Synthesis of graphene oxide (GO)

The preparation of GO was synthesized based on Hummer's method [16]. Briefly, 2 g of purified graphite powder was added into 120 mL of concentrated H₂SO₄/HNO₃ (3:2 v/v) and was stirred for one hour. Next, KMnO₄ (6 g) was slowly added into the mixture and then was stirred for 24 h. Finally, yellow-colored GO was prepared by the existing 3 mL H₂O₂ and 500 g ice.

Synthesis of magnetic graphene oxide (MGO)

Firstly, 1 g of GO, 0.4 g of FeCl₃ 6H₂O, and 0.2 g of (NH₄)₂Fe(SO₄)₂·6H₂O were added into 20 mL deionized water and sonicated at 40 °C. Next, 5 mL of NH₃ (32%) was added to the mixture, and the suspension was stirred for 2 h. The black product was gathered by a magnet, washed three times with distilled water and ethanol, and dried at 80 °C for 24 h.

Synthesis of magnetic graphene oxide/lanthanum phosphate (MGO@LaP)

The LaP was synthesized by the sol-gel method [17]. LaCl₃ 6H₂O (2 g) and H₃PO₄ (2 mL) were mixed in a beaker and stirred for 2 h. Then, distilled water (50 mL) was gradually added to it, and the pH was adjusted within 6.8–7.8 with NH₃ (35%). The sediment was washed with distilled water (70 °C) to eliminate residual chloride ions. The sediment was dispersed into deionized water (50 mL), and the pH was adjusted at 1.8–2.2 with HNO₃ (20%). After stirring (5 h) and ultra-sonication (15 min), the beaker was put under the NH₃ atmosphere for 24 h to rearrange the sol to gel. The gel was dried (70 °C) and calcined at 600 °C for 1 h. Finally, LaP (0.5 g) and MGO (1 g) were added to a mixture of MeOH and water (100 mL, 50:50 v/v) and was sonicated for 1 h to obtain MGO@LaP.

The procedure

The pH of a sample solution containing CPS and HEX (100 mL, 50 µg L⁻¹) was adjusted at 6 ± 0.2 by HCl (0.1 M) and NaOH (0.1 M) solutions. MGO@LaP (10 mg) was sonicated in acetone (1 mL) and distilled water (1 mL) subsequently and then injected into the sample solution. After shaking at 400 rpm for 5 min, MGO@LaP was separated by a handheld magnet and dried under N₂ gas stream. The adsorbed analytes were eluted from MGO@LaP by toluene (1 mL) and vortexing of the solution for 3 min. A magnet removed MGO@LaP from the mixture and the supernatant containing the desorbed pesticides was dried under N₂ gas stream. Finally, the residue was redissolved in 100 µL MeOH, and then 1 µL of it was injected into GC-ECD.

Results and discussion

Characterization

The FTIR spectra of the prepared MGO, LaP, and MGO@LaP nanoparticles are shown in Fig. 1a. The band at 580 cm^{-1} in the spectrum of MGO is ascribed to Fe–O stretching vibrations that indicate the formation of Fe_3O_4 nanoparticles on GO sheets. The peaks at 1003 , 1353 , and 1564 cm^{-1} are assigned to C–O–C, C–OH, and C=C stretching vibrations on GO, respectively. Also, the bands at 3394 cm^{-1} belong to O–H stretching vibrations [18]. In the IR spectrum of LaP, the strong peak at 1360 cm^{-1} can be related to phosphate P–O stretching vibrations, and the peaks at 612 and 532 cm^{-1} are attributed to O=P–O and O–P–O bending vibrations, respectively [19, 20]. The band at 1004 cm^{-1} is assigned to the La–O stretching vibrations [21]. The spectrum of MGO@LaP shows the characteristic peaks of MGO and LaP together.

The magnetic properties of MGO and MGO@LaP were investigated by the VSM technique at ambient temperature. The magnetization hysteresis loops of both substances shown in Fig. 1b are s-shaped and passed through zero-point magnetization, which exhibits superparamagnetic properties. The value of saturation magnetization of MGO and MGO@LaP was equal to ~ 15 and 8 emu/g , respectively. The saturation magnetization of MGO@LaP is lower than MGO, which can be due to the presence of magnetically inactive LaP. However, the results indicate that MGO@LaP exhibits good magnetic property and can be separable from sample solutions using a handheld magnet.

In order to assess the morphology details of the MGO@LaP nanocomposite, it was analyzed by the FE-SEM technique. Figure 1c shows the SEM micrograph of the relatively uniform nanostructure of LaP nanoparticles with an average diameter of $\sim 20\text{ nm}$ (ImageJ software, version 1.51, LOCI, University of Wisconsin, USA). The SEM image of MGO shows that the iron oxide nanoparticles are uniformly dispersed on the surface of GO sheets (Fig. 1d). The image of MGO@LaP indicates that the LaP particles are doped on the surface of MGO (Fig. 1e). It shows that the LaP particles, Fe_3O_4 , and GO sheets are integrated into the unit.

The chemical composition of MGO@LaP was characterized by EDX mapping analysis, and the results in Fig. 1f confirm the formation of the target nanocomposite. The crystalline structure of prepared nanocomposite was investigated with XRD technique. The proposed pattern (Fig. 2) shows that the adsorbent has a good crystalline nature due to various diffraction signals at 2θ in the range of 15° to 70° . The signals at 18.93° , 21° , 26.87° , 28.63° , 30.92° , 34.01° , 41.41° , 52.32° , and 70.66° are corresponding to LaP nanoparticles. This pattern is similar with the previously published diffraction for LaP nanoparticles [17]. XRD diffractions for graphene oxide are observed at $\sim 15^\circ$ and 40° , and for magnetic nanoparticles are observed at 2θ of 25.11° , 30.01° , 35.98° , 44.17° , 51.16° , 56.09° , and 60.81° . Hence, the sharp diffractions demonstrated crystalline structure of synthesized MGO@LaP nanocomposite.

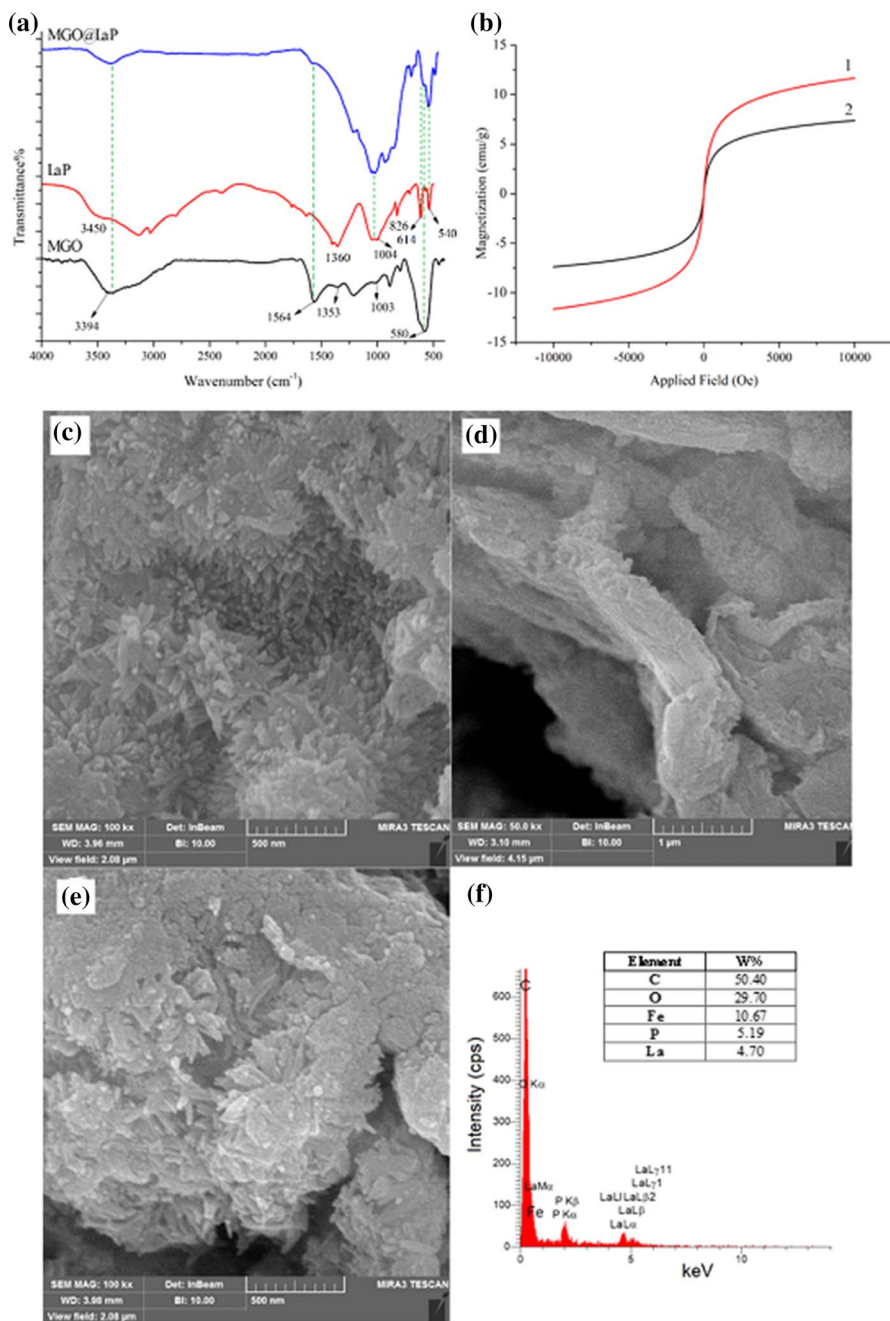


Fig. 1 **a** The FTIR spectra of magnetic graphene oxide (MGO) nanocomposite, lanthanum phosphate (LaP) nanoparticles, and MGO@LaP nanocomposite; **b** The VSM magnetization curve of (1) MGO and (2) MGO@LaP; The SEM micrograph of **c** LaP; **d** MGO; and **e** MGO@LaP; **f** The EDX spectrum of MGO@LaP

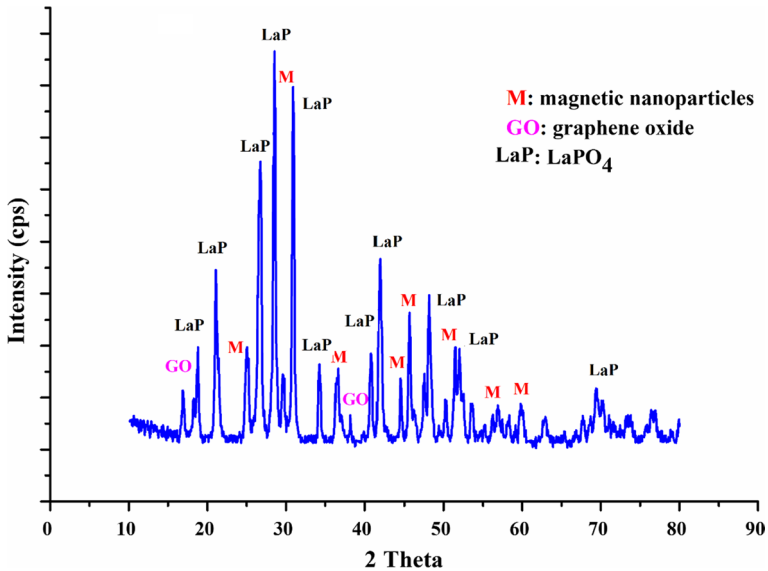


Fig. 2 The X-ray diffraction (XRD) pattern of the adsorbent (MGO@LaP)

Optimization of the extraction procedure

Effect of desorption conditions

Effective desorption of the adsorbed analytes from the surface of MGO@LaP is obtained by a suitable organic solvent. The organic solvent should be capable of simultaneous elution of the target analytes quantitatively using minimum volume without damaging the adsorbent material [22]. For this purpose, six organic solvents of different polarities namely MeOH, ACN, acetone, toluene, MeOH/toluene (50:50 v/v), and *n*-hexane were tested according to the procedure, and the results are shown in Fig. 3a. Although toluene and MeOH are the most efficient for desorption of HEX and CPS, respectively, but comparing the efficiencies of these two solvents, toluene is capable of simultaneous desorption of both analytes more efficiently. Therefore, toluene was used as a desorption solvent. Moreover, the volume of toluene is another desorption parameter to attain reliable and reproducible analytical results [23]. The influence of volume toluene on the extraction efficiency was investigated in the range of 0.5–5.0 mL. As shown in Fig. 3b, the peak areas increased from 0.5 to 1 mL and then remained almost constant. Therefore, 1 mL of toluene was considered as the optimum desorption volume. Finally, the effect of desorption time was examined in the range of 1–10 min. In order to accelerate the desorption process, the sample solution was vortexed. Figure 3c shows that after 3 min of desorption, a decrease in peak areas was observed. Since adsorption/desorption is an equilibrium process, this decrease is probably due to the re-adsorption of analytes onto the adsorbent [24]. Based on this, 3 min was enough to accomplish the desorption of

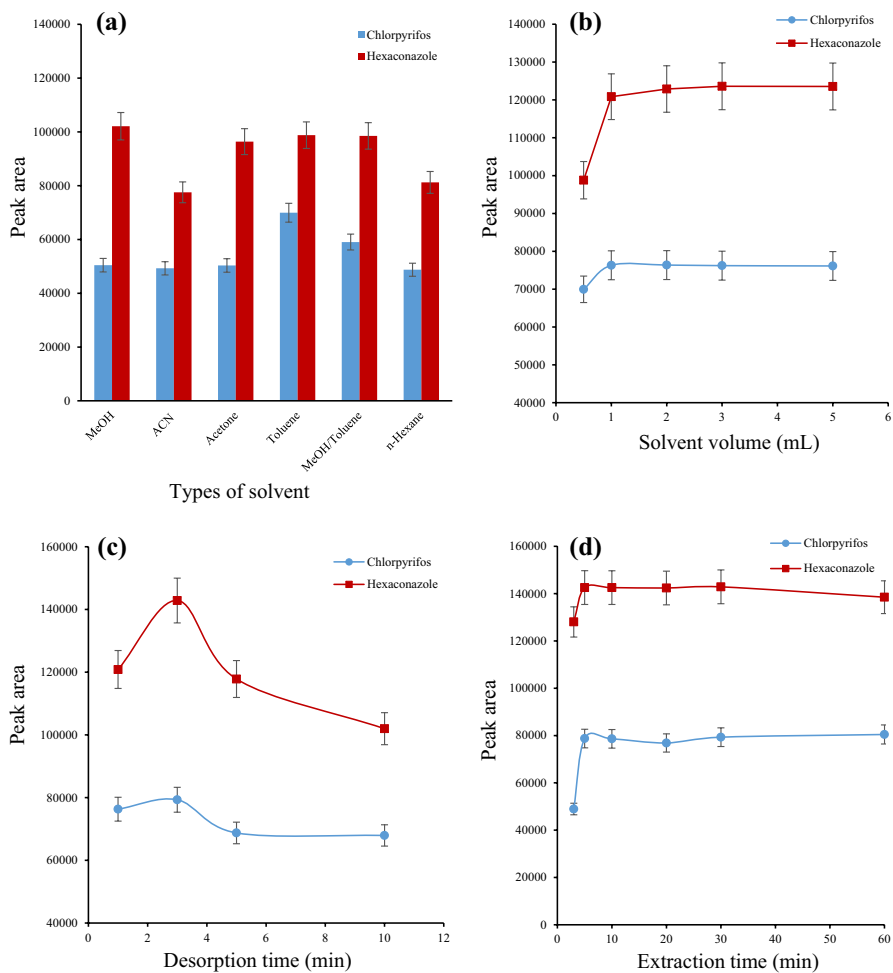


Fig. 3 Effect of **a** desorption solvent type; **b** desorption solvent volume; **c** desorption time, and **d** extraction time on the extraction efficiency. (Concentration of CPS and HEX: $50 \mu\text{g L}^{-1}$)

analytes from the adsorbent. Finally, the analytes were desorbed with 1 mL toluene for 3 min for the following experiments.

Effect of extraction time

MSPE is not a tedious extraction method but partition equilibrium process of the analytes between adsorbent and sample solution, which requires sufficient contact time to achieve the adsorption equilibrium. In order to accelerate the partition equilibrium and improve the mass transfer of analytes from the aqueous phase to the adsorbent, extraction procedure is performed by shaking of sample solution [23, 25]. Thus, the influence of extraction time on the efficiency was investigated in

the 3–60 min range. Figure 3d shows that the maximum efficiency was obtained at 5 min. The relatively fast equilibrium time could be attributed to the large available specific area of the adsorbent and the rapid mass transfer of the target analytes in the solution. Therefore, 5 min was chosen as the optimum extraction time.

Effect of adsorbent amount

The amount of adsorbent influences the extraction efficiency by providing more surface area and accessible active sites for adsorption. The effect of the parameter on the efficiency was studied in the range of 5–30 mg of MGO@LaP. The results show that by increasing the amount of MGO@LaP up to 10 mg, the efficiency increased and then remained almost constant (Fig. 4a). Hence, 10 mg was selected as the optimum adsorbent amount in the subsequent experiments.

Effect of pH

The pH of the sample solution can affect the chemical form of target analytes and the surface charge of the adsorbent [26]. The effect of pH on the extraction efficiency was investigated in the range of 2–10, adjusting by HCl (0.1 M) or NaOH (0.1 M) solutions. As shown in Fig. 4b, the highest peak areas for the extracted analytes were obtained when the pH value was 6. Since CPS and HEX may be hydrolyzed at strongly acidic and basic pHs, the peak areas of the extracted analytes were dramatically decreased in both domains [27, 28].

Furthermore, considering zeta potential analysis at pH 6 (+20 mV), the surface of MGO@LaP is positively charged while the analytes (CPS (no pKa) [29] and HEX (pKa=2.7) [30]) are negatively charged. Consequently, the highest peak areas at pH 6 may be attributed to electrostatic interactions between the positively charged surface of the adsorbent and negatively charged analytes. Besides, La^{3+} provides electrostatic affinity toward electronegative atoms of the analytes (O, Cl, N, and S). Also, at pH 6, hydrogen bonding and π – π interactions between the adsorbent and the analytes can improve extraction efficiency. The possible interactions are shown in Fig S1 (supplementary data file).

Effect of salt amount

In general, the addition of salt into the sample solution can increase extraction efficiency by reducing the solubility of the analytes in the aqueous sample and thus improving their partitioning into the organic phase. However, in some cases, extraction efficiency is reduced due to the decrease in the diffusion rate of the analytes from the sample solution to the adsorbent [31]. Different amounts of NaCl (0–10 w/v%) was added to the sample solution and tested according to the procedure. Based on the results shown in Fig. 4c, adding salt led to a decrease in extraction efficiency. Thus, further experiments were performed without adding salt to the sample solutions.

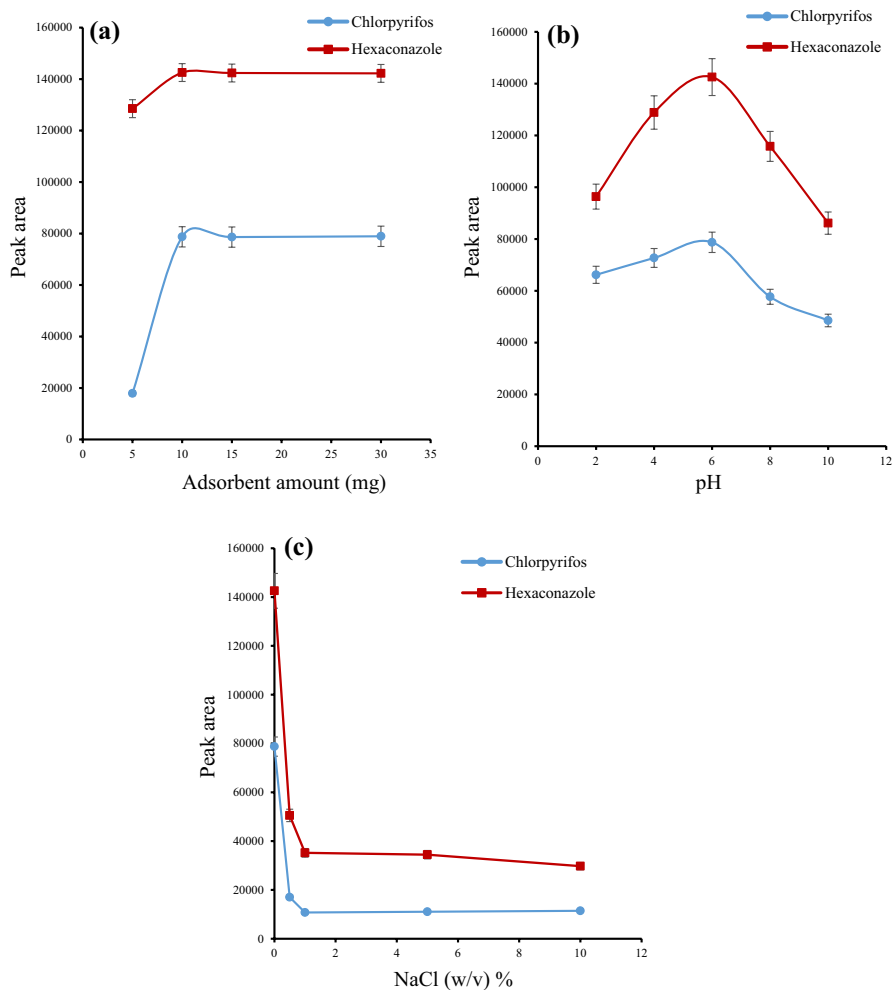


Fig. 4 Effect of **a** adsorbent amount, **b** solution pH, and **c** salt concentration on the extraction efficiency. (Concentration of CPS and HEX: $50 \mu\text{g L}^{-1}$)

Method validation

The developed MD- μ -SPE/GC-ECD method was validated by obtaining its analytical figures of merit under the optimal conditions (desorption solvent (toluene), 1 mL; desorption time, 3 min; extraction time, 5 min; adsorbent amount, 10 mg; and pH, 6). The related results were summarized in Table 1. The matrix-matched calibration curve was constructed using the standard solutions of the selected pesticides at nine concentration levels (1 – $1500 \mu\text{g L}^{-1}$). The linear dynamic range (LDR) for both pesticides was obtained 3 – $1500 \mu\text{g L}^{-1}$ with good determination coefficients of (R^2) > 0.997 . The limits of detection (LOD) based on the signal to noise ratio (S/N)

Table 1 The analytical figures of merit of the MD- μ -SPE/GC-ECD method for the determination of the selected pesticides

Analytes	LOD ^a	LOQ ^b	LDR ^c	R^2 ^d	RSD ^e %	
					Intra-day ($n=3$)	Inter-day ($n=9$)
Chlorpyrifos	0.67	2.22	3–1500	0.997	4.0	5.6
Hexaconazole	0.89	2.94	3–1500	0.998	2.3	3.3

^aLimit of detection ($\mu\text{g L}^{-1}$)^bLimit of quantification ($\mu\text{g L}^{-1}$)^cLinear dynamic range ($\mu\text{g L}^{-1}$)^dCoefficient of determination^eRelative standard deviation ($C=10 \mu\text{g L}^{-1}$ each pesticide)

of 3 were obtained equal to 0.67 and 0.89 $\mu\text{g L}^{-1}$ for CPS and HEX, respectively. The limits of quantification (LOQ) ($S/N=10$) were 2.22 for CPS and 2.94 $\mu\text{g L}^{-1}$ for HEX. Therefore, the obtained LOQ is below the MRLs defined by EU regulations. The intra-day ($n=3$) and inter-day ($n=9$) precisions based on the relative standard deviation percentage (RSD%) were calculated using a standard solution at the concentration level of 10 $\mu\text{g L}^{-1}$ for each analyte. The intra-day and inter-day RSDs were 2.3–4.0 and 3.3–5.6, respectively.

The reusability of MGO@LaP was investigated by several consecutive cycles under optimum conditions. After any cycle, MGO@LaP was washed by acetone (1 mL) and distilled water (1 mL) and then dried to reuse in the next extraction. The results showed that MGO@LaP could be reused for nine times with no significant reduction (<5%) in extraction efficiency.

Analysis of real samples

In order to evaluate the applicability of the proposed method, three kinds of real samples (tap water sample, pineapple, and orange juices) were selected and analyzed for the determination of the pesticides. The water sample was taken from the university campus, and the natural fruit juices were purchased from a local supermarket in Tehran (Iran). All fruit juices were filtered through a 0.45 μm membrane filter to remove suspended solid particulates before the extraction procedure. For all real samples (tap water sample, pineapple, and orange juices), 100 mL of the sample was analyzed according to the extraction procedure. The results showed that no target analytes were detectable in the real samples. Also, the samples were spiked at 10 and 30 $\mu\text{g L}^{-1}$ of each pesticide and analyzed by the procedure. The relative recoveries (RR) were obtained for the evaluation of the method accuracy using Eq. (1):

$$\text{RR}\% = \frac{C_{\text{spiked}} - C_{\text{real}}}{C_s} \times 100 \quad (1)$$

where C_{spiked} is the concentration of the analyte in the real sample spiked with a standard solution, C_{real} is the concentration of the analyte in the unspiked real sample, and C_s is the concentration of the standard solution. The results given in Table 2 showed that the recoveries were in the range of 78–120% with low RSDs (below 4.5%). Therefore, regarding these data, it can be deduced that the proposed method can be used for the detection of pesticide residues in the samples with various matrices, including water and complex fruit juice matrices. Figure 5 shows the representative chromatograms of the unspiked and spiked fruit juices.

Comparison with other methods

The performance of the proposed MD- μ -SPE/GC-ECD method based on MGO@LaP as adsorbent was compared with other SPE-based methods in the literature for the determination of pesticides [28, 32–35]. As shown in Table 3, the introduced method provided satisfactory precision and linearity, low detection limits, and good recovery compared with most of the mentioned methods. Although detection limits in HS-SPME/GC-MS are low, it can be explained by the highly sensitive and

Table 2 Evaluation of MD- μ -SPE/GC-ECD accuracy at two concentrations of 10 and 30 ($\mu\text{g L}^{-1}$)

Sample	Chlorpyrifos	Hexaconazole
Orange juice \pm SD ^a ($\mu\text{g L}^{-1}$)	n.d	n.d
Added ($\mu\text{g L}^{-1}$)	10	10
Found \pm SD ($\mu\text{g L}^{-1}$)	8.2 ± 0.33	10.8 ± 0.29
Rel. recovery ^b %	82	108
Added ($\mu\text{g L}^{-1}$)	30	30
Found \pm SD ($\mu\text{g L}^{-1}$)	36 ± 1.44	34.8 ± 0.87
Recovery %	120	116
Pineapple juice \pm SD ($\mu\text{g L}^{-1}$)	n.d	n.d
Added ($\mu\text{g L}^{-1}$)	10	10
Found \pm SD ($\mu\text{g L}^{-1}$)	9.9 ± 0.41	7.8 ± 0.17
Recovery %	99	78
Added ($\mu\text{g L}^{-1}$)	30	30
Found \pm SD ($\mu\text{g L}^{-1}$)	24 ± 0.98	27.2 ± 0.71
Recovery %	80	90
Water \pm SD ($\mu\text{g L}^{-1}$)	n.d	n.d
Added ($\mu\text{g L}^{-1}$)	10	10
Found \pm SD ($\mu\text{g L}^{-1}$)	9.7 ± 0.40	10.42 ± 0.24
Recovery %	97	104
Added ($\mu\text{g L}^{-1}$)	30	30
Found \pm SD ($\mu\text{g L}^{-1}$)	31.2 ± 1.21	32.43 ± 0.76
Recovery %	104	108

Each analysis repeated for three times ($n=3$)

^aStandard deviation

^bRelative recovery percent

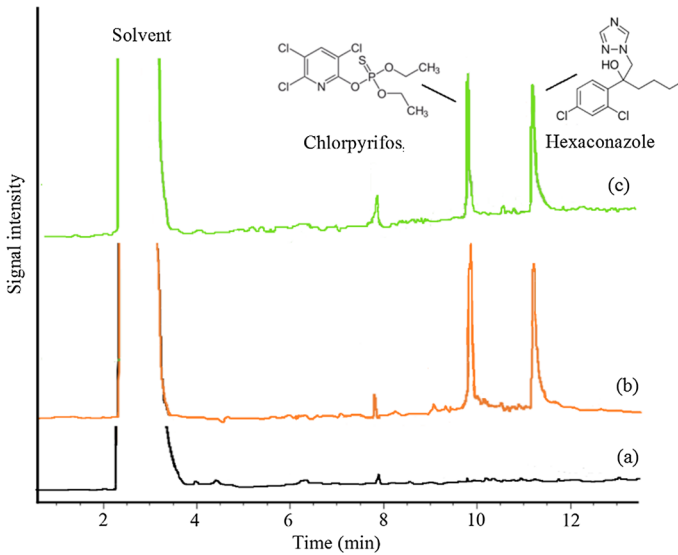


Fig. 5 The GC-ECD representative chromatograms of **a** unspiked sample, **b** spiked pineapple juice, and **c** spiked orange juice. (1) CPS, and (2) HEX (each at the concentration level of $30 \mu\text{g L}^{-1}$)

selective detection systems. Besides, the developed method used a lower amount of adsorbent than other methods, which can be related to the high adsorption capacity of MGO@LaP. Moreover, the method showed a very short extraction time due to hydrogen bonding, hydrophobicity, π - π stacking, and electrostatic interactions between the adsorbent and target analytes. These results show that MD- μ -SPE/GC-ECD method is fast, simple, and effective for the determination of pesticides from various matrices.

Conclusions

In this present work, magnetic graphene oxide (MGO)-based adsorbent decorated by LaP was synthesized and used as an efficient adsorbent for the extraction of pesticides. Due to high surface area, high adsorption capacity, low consumption of adsorbent, highly efficient interactions with the target analytes, good recovery, easy synthesis method, low cost, and environment friendly, MGO@LaP was considered as an interesting MD- μ -SPE adsorbent for extraction of pesticides from water and fruit juice matrices. Furthermore, the introduced method indicated satisfactory precision and linearity and low detection limits. According to the results, good performance of adsorbent in simple and complex matrices can be related to the combination of both MGO and LaP structural features, which lead to the formation of hydrogen bonding, hydrophobicity, electrostatic, and π - π stacking interactions. Considering the results, the nanocomposite as a useful adsorbent can exhibit high adsorption capacity for the extraction of pesticides in various matrices.

Table 3 Comparison between the current MD- μ -SPE/GC-ECD method and previously reported methods for the determination of pesticides

Analyte	Sample	Method	LOD ($\mu\text{g L}^{-1}$)	LDR ($\mu\text{g L}^{-1}$)	RSD (%)	RR (%)	Extraction time (min)	Sorbent (mg)	Refs.
Chlorpyrifos, hexaconazole	Fruit juices natural water	MD- μ -SPE ³ /GC-ECD ^b	0.67, 0.89	3–1500	2.3–5.6	78–116	13	10	This work
Penconazole, hexaconazole, diniconazole, tebuconazole, triticonazole, difenconazole	Aqueous samples	SBSE/DLLME ^c /GC-FID ^d	0.53–24	10–50,000	2.9–5.2	71–102	32	100	[28]
Diazinon, ametryn, chlorpyrifos, enconazole, oxadiazon, diniconazole, fenaziquin	Fruit juices	MDSPE ^e -DLLME/GC-FID	0.15–0.33	0.49–5000	2–6	88–97	10	200	[32]
Diazinon, quinalphos, chlorpyrifos	Fruit sample natural water	SPE/HPLC	0.83–2.8	1–250	0.8–1.47	91–99	> 30	–	[33]
Penconazole, hexaconazole, diniconazole, tebuconazole, triticonazole, difenoconazole		HS-SPME ^f /GC-MS	0.01–0.09	0.1–2000	4.3–9.2	–	–	–	[34]
Ethoprophos, diazinon, chlorpyrifos-methyl, fenitrothion, malathion, chlorpyrifos, fenamiphos, buprofezin, triphenylphosphate	Fruit juices	SPE/GC-NPD ^g	1.85–7.32	57–1680	< 8.3	73–103	> 20	40	[35]

^aMagnetic dispersive microsolid-phase extraction^bGas chromatography–electron capture detection^cStir bar sorptive extraction/dispersive liquid–liquid microextraction^dGas chromatography–flame ionization detection^eMagnetic dispersive solid-phase extraction^fHeadspace solid-phase microextraction^gGas chromatography–nitrogen–phosphorus detection

Compliance with ethical standards

Conflict of interest The authors declare that they have no financial/commercial conflicts of interest.

Ethical approval This article does not contain any studies with human or animal studies.

References

1. J. Fenik, M. Tankiewicz, M. Biziuk, *Trends Anal. Chem.* **30**(6), 814 (2011)
2. K.H. Kim, E. Kabir, S.A. Jahan, *Sci. Total Environ.* **575**, 525 (2017)
3. G. Satpathy, Y.K. Tyagi, R.K. Gupta, *Food Chem.* **127**, 1300 (2011)
4. EU, Regulation (EC) No 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC (1), *Off. J. Eur. Union.* (2018) 6
5. D.A. Varela-Martínez, M.Á. González-Curbelo, J. González-Sálamo, J. Hernández-Borges, *Food Chem.* **297**(124961), 1 (2019)
6. Y. Wang, C. Chen, X. Cao, J. Li, *Res. Chem. Intermed.* **41**(5), 2841 (2015)
7. A. Samsidar, S. Siddiquee, S.M. Shaarani, *Trends Food Sci. Technol.* **71**, 188 (2018)
8. P. Zhao, Z. Wang, X. Gao, X. Guo, L. Zhao, *Food Chem.* **277**, 298 (2019)
9. W.A. Wan Ibrahim, H.R. Nodeh, H.Y. Aboul-Enein, M.M. Sanagi, *Crit. Rev. Anal. Chem.* **45**(3), 270 (2015)
10. M.A. Farajzadeh, R. Safi, A. Yadeghari, *Microchem. J.* **147**, 571 (2019)
11. D. Li, M. He, B. Chen, B. Hu, *J. Chromatogr. A* **1583**, 19 (2019)
12. M. Skandarpour, P. Jamshidi, M.R. Moghaddam, J. Ghasemi, F. Shemirani, *Res. Chem. Intermed.* **45**, 3141 (2019)
13. R. Sitko, B. Zawisza, E. Malicka, *Trends Anal. Chem.* **51**, 33 (2013)
14. F. Movahedi, H. Masroui, H. Tayyebi, *Res. Chem. Intermed.* **44**(9), 5419 (2018)
15. S. Sankar, G.P.V. Prajeesh, V.N. Anupama, B. Krishnakumar, P. Hareesh, B.N. Nair, K.G. Warriar, U.N.S. Hareesh, *J. hazard. Mater.* **275**, 222 (2014)
16. W.S. Hummers Jr., R.E. Offeman, *J. Am. Chem. Soc.* **80**(6), 1339 (1958)
17. S. Sankar, K.G. Warriar, *J. Sol-Gel Sci. Technol.* **58**, 195 (2011)
18. L. Li, L. Fan, M. Sun, H. Qiu, X. Li, H. Duan, C. Luo, *Colloids Surf. B* **107**, 76 (2013)
19. K. Rajesh, P. Shajesh, O. Seidel, P. Mukundan, K.G.K. Warriar, *Adv. Funct. Mater.* **17**, 1682 (2007)
20. L. Xu, H. Song, B. Dong, Y. Wang, X. Bai, G. Wang, Q. Liu, *J. Phys. Chem. C* **113**, 9609 (2009)
21. H. Rashidi Nodeh, H. Sereshti, E.Z. Afsharian, N. Nouri, *J. Environ. Manag.* **197**, 265 (2017)
22. B. Arabsorkhi, H. Sereshti, A. Abbasi, *Sep. Sci. J.* **42**, 1500 (2019)
23. S. Mahpishanian, H. Sereshti, *J. Chromatogr. A* **1485**, 32 (2017)
24. L.M. Aow Yong, K. Wmawm, F. Yusoff, S.H. Loh, *Res. J. Chem. Environ.* **23**(5), 10 (2019)
25. N. Li, J. Chen, Y.P. Shi, *Talanta* **141**, 212 (2015)
26. C. Liu, X. Liu, P.J. Marriott, H. Qian, Z. Meng, Z. Yang, R. Lu, H. Gao, W. Zhou, *J. Sep. Sci.* **42**(8), 1610 (2019)
27. N. Rahbar, E. Behrouz, Z. Ramezani, *Food Anal. Methods* **10**, 2229 (2017)
28. M.A. Farajzadeh, D. Djozan, N. Nouri, M. Bamorowat, M.S. Shalamzari, *J. Sep. Sci.* **33**, 1816 (2010)
29. M. Svobodová, K. Šmídová, M. Hvězdová, J. Hofman, *Environ. Pollut.* **236**, 257 (2018)
30. Z. Wang, J. Zhang, B. Hu, J. Yu, J. Wang, X. Guo, *J. Taiwan Inst. Chem. Eng.* **95**, 635 (2019)
31. S. Mahpishanian, H. Sereshti, M. Baghdadi, *J. Chromatogr. A* **1406**, 48 (2015)
32. M.A. Farajzadeh, A. Mohebbi, *J. Chromatogr. A* **1532**, 10 (2017)
33. M.M. Sanagi, S. Salleh, W.A.W. Ibrahim, A.A. Naim, D. Hermawan, M. Miskam, I. Hussain, H.Y. Aboul-Enein, *J. Food Compos. Anal.* **32**, 155 (2013)
34. M.M. Abolghasemi, S. Hassani, M. Bamorowat, *Microchim. Acta* **183**, 889 (2016)
35. L.M. Ravelo-Pérez, J. Hernández-Borges, M.Á. Rodríguez-Delgado, *J. Chromatogr. A* **1211**, 33 (2008)

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