

# Microwave-assisted synthesis of reduced graphene oxide decorated with magnetite and gold nanoparticles, and its application to solid-phase extraction of organochlorine pesticides

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**Abstract** An agent-free microwave-assisted method was developed for the preparation of a reduced graphene oxide/ $\text{Fe}_3\text{O}_4$ @gold nanocomposite. This material was used as an adsorbent for magnetic solid-phase extraction of organochlorine pesticides (OCPs) from water samples. The nanocomposite was characterized by transmission electron microscopy, scanning electron microscopy, Fourier transform infrared spectroscopy and energy-dispersive X-ray spectroscopy. The effects of sample volume, amount of sorbent, eluent volume, extraction and desorption time, and the effect of salt on the extraction efficiency were optimized. The linear response range of GC analysis extends from 0.05 to 500  $\mu\text{g L}^{-1}$  of OCPs, the limits of detection range from 0.4 to 4.1  $\text{ng L}^{-1}$ , relative standard deviations from 1.7 to 7.3 %, and recoveries (from spiked seawater samples) from 69 to 114 %.

**Keywords** Magnetic nanoparticles · Gas chromatography · Heptachlor · Aldrin · Dieldrin · DDD · DDT

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## Introduction

Magnetic solid-phase extraction (MSPE) is based on the adsorption of target analyte(s) on a magnetic adsorbent. Generally, in this procedure the extraction can be performed in an easy way, and it can save the time, without any need to the expensive equipment and large volume of the eluent. The adsorbed analyte(s) can be easily separated by an external magnetic field.

Until now different adsorbents have been reported. Carbon-based nanomaterials have been appeared as a strong coating due to their remarkable electronic properties and excellent mechanical, electrical and chemical properties [1]. Graphene recently is one of the most widely used carbon-based nanomaterials. Graphene has been attracted great attention as a sorbent due to its great properties such as large surface area, high adsorption capacity [2], and its usability in small quantities. The graphene-based MSPE have been used in various fields such as environmental analysis, food safety analysis and bio-analysis. Luo et al. [3] used magnetic graphene as a sorbent for extraction of sulfonamide antibiotics. Han et al. [4] reported a MSPE method based on the  $\text{Fe}_3\text{O}_4$ /graphene oxide (GO) for preconcentration of several polycyclic aromatic hydrocarbons in water samples.

Bare graphene sheets tend to agglomerate or restack to form graphite, if the sheets are not separated well [5]. It would reduce their surface area. Chemical modification of graphene can develop its properties. Graphene is usually non-polar and hydrophobic material. But graphene oxide contains much more polar moieties, and thus has a more polar and hydrophilic character than graphene [6]. In addition pristine magnetic nanoparticles (MNPs) can be aggregated, resulting in a reduction in the magnetic properties [7]. Graphene oxide sheets are negatively charged when dispersed in aqueous solution. The composition of Iron (III) oxide and graphene can be formed

through the electrostatic interaction, because  $\text{Fe}_3\text{O}_4$  has a positively charged surface in aqueous solutions [8]. Functional groups, such as carboxyl ( $-\text{COOH}$ ), carbonyl ( $-\text{CO}$ ), and hydroxyl ( $-\text{COH}$ ) groups, connect GO to magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles through chemical bonds [9]. Thus composite of  $\text{Fe}_3\text{O}_4/\text{GO}$  can overcome the above limitations. The presence of  $\text{Fe}_3\text{O}_4$  NPs on the GO surface may reduce its effective surface area and effect on its adsorption capacity.

Gold nanoparticles (Au-NPs) have many important properties such as chemical stability, biocompatibility, magnetic properties and ease of chemical modification [10]. Application of Au-NPs as stationary phases obtained high separation efficiencies for a variety of analytes [11]. The combination of Fe and Au, such that iron or iron oxide as core and gold as shell, is attractive because of the fantastic properties of gold. A lot of studies focus on Fe–Au core–shell NPs [12]. Stoeva et al. [13] have used  $\text{Fe}_3\text{O}_4$  and gold as the inner and outer shell for silica core. Several studies have also been used Au-NPs without any treatment or improvement for practical application [14]. The benefits of  $\text{Fe}_3\text{O}_4$ -Au composite increased its application such as using as probes for DNA [15], protein separation [16], catalysis [17], and adsorption [18]. Coating of gold nanoparticles as a novel metal onto graphene sheets can act as an operative sorbent for solid phase extraction. The aurum atom of gold nanoparticles can cause  $\pi$  interaction with the analytes through the  $\pi$ -conjugated system [19]. Also, they can bind with a large range of organic molecules such as molecules containing thiol and amino groups [20].

Organochlorine pesticides (OCPs) have been widely used in around the world [21]. Most of them are hydrophobic and remain in marine environment and can accumulate in biological organisms [22]. It has been reported that OCPs may influence the function of human and wildlife endocrine system [23]. There are several mechanisms that result in the deposition of OCPs in the environment such as urban runoff, industrial waste, chemical spills, outflow from agricultural areas and etc. [24].

In this work, the reduced graphene oxide/ $\text{Fe}_3\text{O}_4$ @ Au-NPs composite (RGO/ $\text{Fe}_3\text{O}_4$ @Au) was synthesized with a simple microwave-assisted method and used for extraction of OCPs, as model compounds, in the natural water samples.

## Experimental

### Chemicals and reagents

Iron (III) chloride hexahydrate ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), iron (II) chloride tetrahydrate ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), sulfuric acid (98 %), phosphoric acid (85 %), potassium permanganate ( $\text{KMnO}_4$ ), graphite powder (99.9 %) and ammonia ( $\text{NH}_3$ ) were purchased from Merck (Darmstadt, Germany, [www.merckmillipore.com](http://www.merckmillipore.com)).

Acetonitrile (HPLC grade) and hydrogen tetrachloroaurate (III) trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) were purchased from Samchun Co. (Seoul, Korea, [www.samchun.com](http://www.samchun.com)) and Acros Organics (Noisy-le-Grand, France, [www.acros.com](http://www.acros.com)), respectively.

The OCPs (Heptachlor, Aldrin, p,p' - DDE, Dieldrin, p,p' - DDD and p,p' - DDT) standards were purchased from Sigma-Aldrich (Milan, Italy, [www.sigmaldrich.com](http://www.sigmaldrich.com)). The stock standard solutions of OCPs were prepared in acetonitrile at a concentration of  $100 \mu\text{g mL}^{-1}$ . The working solutions were daily prepared by diluting the stock standard solution with deionized water.

### Apparatus

An Agilent 6890 N gas chromatograph (Wilmington, DE, USA, [www.agilent.com](http://www.agilent.com)) equipped with a split/splitless inlet and micro-electron capture detector ( $\mu$ -ECD) was used for the determination of OCPs. The injector and detector temperatures were 260 and 300 °C, respectively. The carrier gas was  $\text{N}_2$  (99.999 %, [www.roham.com](http://www.roham.com)) with the flow rate of  $1.2 \text{ mL min}^{-1}$ . Chromatographic separation was accomplished with a HP-5 (5 % biphenyl +95 % polydimethylsiloxane) fused-silica column ( $30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \mu\text{m}$ ). The GC oven was programmed as follow: 100 °C, ramp to 220 °C at  $20 \text{ }^\circ\text{C min}^{-1}$  and held for 0.5 min, after that ramp to 230 °C at  $2 \text{ }^\circ\text{C min}^{-1}$  and held for 3 min, then ramp to 260 °C at  $20 \text{ }^\circ\text{C min}^{-1}$  and then held for 2 min.

The gas chromatography–mass spectrometry (GC–MS) analysis was also performed using a model 6890 N network GC system (Agilent, USA) equipped with a 5973 mass selective detector (Agilent, USA) and HP-5MS fused silica capillary column ( $30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$ ). The GC–MS oven temperature program was the same as the GC oven temperature program. He (99.999 %) was used as the carrier gas at a flow rate of  $1.2 \text{ mL min}^{-1}$ . The injector and auxiliary temperatures were set at 260 and 280 °C, respectively. The acquisition mode of GC–MS was scan mode.

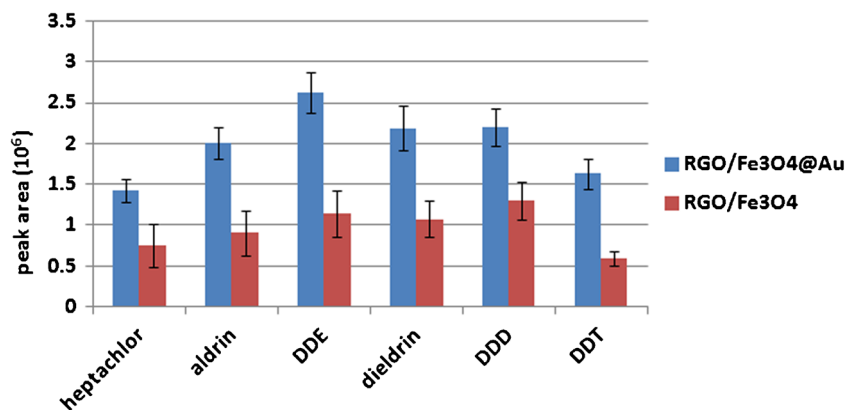
An ETHOS 1 Milestone ([www.milestonesci.com](http://www.milestonesci.com)) closed vessel microwave digestion was used for synthesis of RGO/ $\text{Fe}_3\text{O}_4$ @Au. The program was the microwave radiation at 150 °C for 1 h with 400 W powers.

### Preparation of the sorbent

#### Preparation of graphene oxide

For preparation of graphene oxide (GO), 360 mL  $\text{H}_2\text{SO}_4$  and 40 mL  $\text{H}_3\text{PO}_4$  were mixed. The resulting solution was held on a stirrer and 3 g graphite powder was added into the mixture slowly. Then, 18 g  $\text{KMnO}_4$  was added into the mixture in the ice bucket very slowly. After that, the resulting product was placed in a flask under stirring while the temperature was held

**Fig. 1** Comparison of the extraction efficiencies of reduced graphene/Fe<sub>3</sub>O<sub>4</sub> and reduced graphene/Fe<sub>3</sub>O<sub>4</sub>@Au



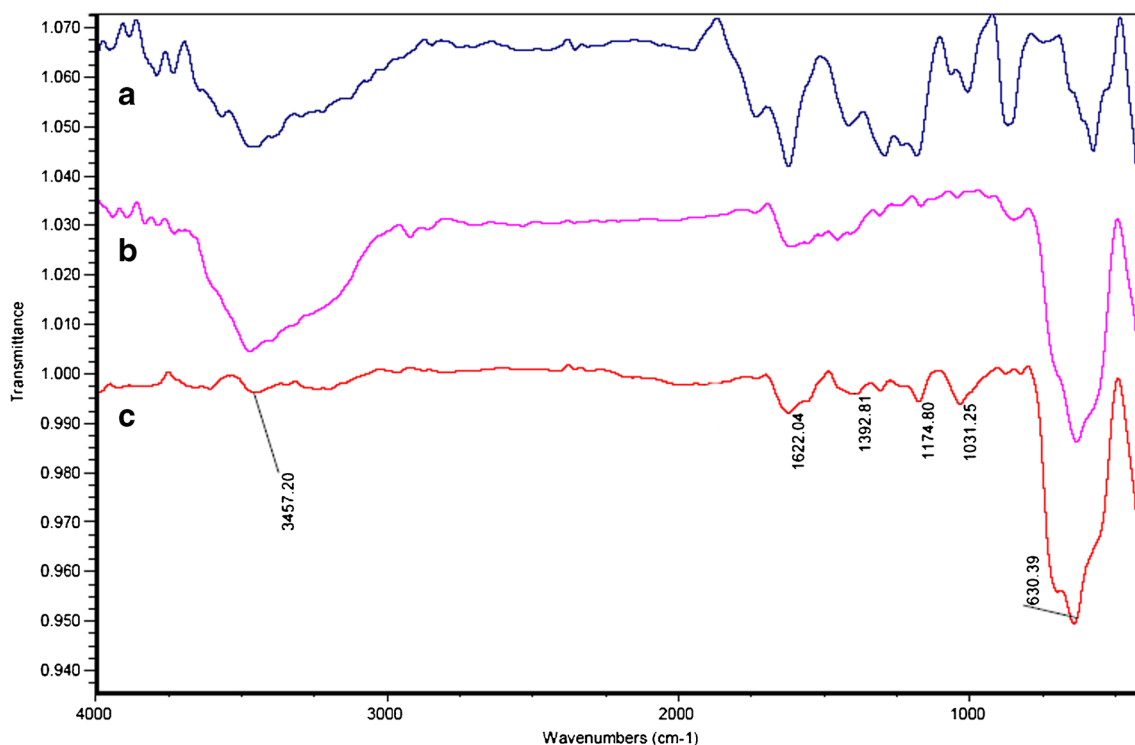
at 50 °C for 24 h. The mixture was washed, centrifuged and placed in an oven for 2 h and then GO was obtained [25].

#### Preparation of RGO/Fe<sub>3</sub>O<sub>4</sub>

For magnetization of GO, 40 mg GO was dissolved in distilled water under sonication for 30 min. Then the product was transferred into a round bottom flask under stirring and nitrogen purge. Next, 800 mg FeCl<sub>3</sub>·6H<sub>2</sub>O and 300 mg FeCl<sub>2</sub>·4H<sub>2</sub>O were added into the flask with 50 mL distilled water and the temperature was increased to 80 °C. 10 mL ammonia was added into the mixture and the resulting product was held under stirring for 30 min. Then the magnetic RGO was washed with distilled water and placed in an oven for 2 h and finally gathered by a magnetic field [26].

#### Preparation of RGO/Fe<sub>3</sub>O<sub>4</sub>@Au

When the initial amount of HAuCl<sub>4</sub> reaches to 20 mg, the Au NPs loaded on the GO sheet tend to aggregate together [27]. Nevertheless, to increase the percentage of Au in the sorbent composition, more than 20 mg HAuCl<sub>4</sub> was used in this work. One mL aqueous solution containing 36 mg HAuCl<sub>4</sub>·3H<sub>2</sub>O was added to 130 mg RGO/Fe<sub>3</sub>O<sub>4</sub> in 75 mL distilled water. The mixture was transferred into a flask under stirring for 2 h and the temperature was held at 60 °C, during which time the Au seed crystals were deposited on the G sheets. Then 1 mL HAuCl<sub>4</sub> solution was once again added into the mixture under stirring [28]. Afterward, the product was transferred into 60 mL Teflon-lined autoclave and heated in an ETHOS 1 closed vessel microwave digestion at 150 °C for 60 min with



**Fig. 2** FTIR spectra of reduced graphene (a), reduced graphene/Fe<sub>3</sub>O<sub>4</sub> (b) and reduced graphene/Fe<sub>3</sub>O<sub>4</sub>@Au (c)

400 W powers. After that, the autoclave was cooled to room temperature, then the precipitate was washed with distilled water and ethanol several times, and RGO/Fe<sub>3</sub>O<sub>4</sub>@Au was obtained by a magnetic field. Then the product was dried in an oven at 80 °C for 12 h.

### MSPE procedure

20 mg RGO/Fe<sub>3</sub>O<sub>4</sub>@Au and 0.5 g NaCl was added to a container containing 10 mL water. The analytes adsorption was occurred on the sorbent under stirring for 10 min. After that, the water solution was separated with an external magnet (1.4 T). The analytes were eluted from the sorbent with 250 µL acetonitrile under stirring for 2 min. 1 µL of eluted solution was injected to the GC-µECD.

### Sample collection

Sea water sample was collected from Caspian Sea (Mazandaran province, Iran). The water sample was filtered through a 0.45 µm membrane filter and stored in dark at 4 °C until used for the analysis.

## Results and discussion

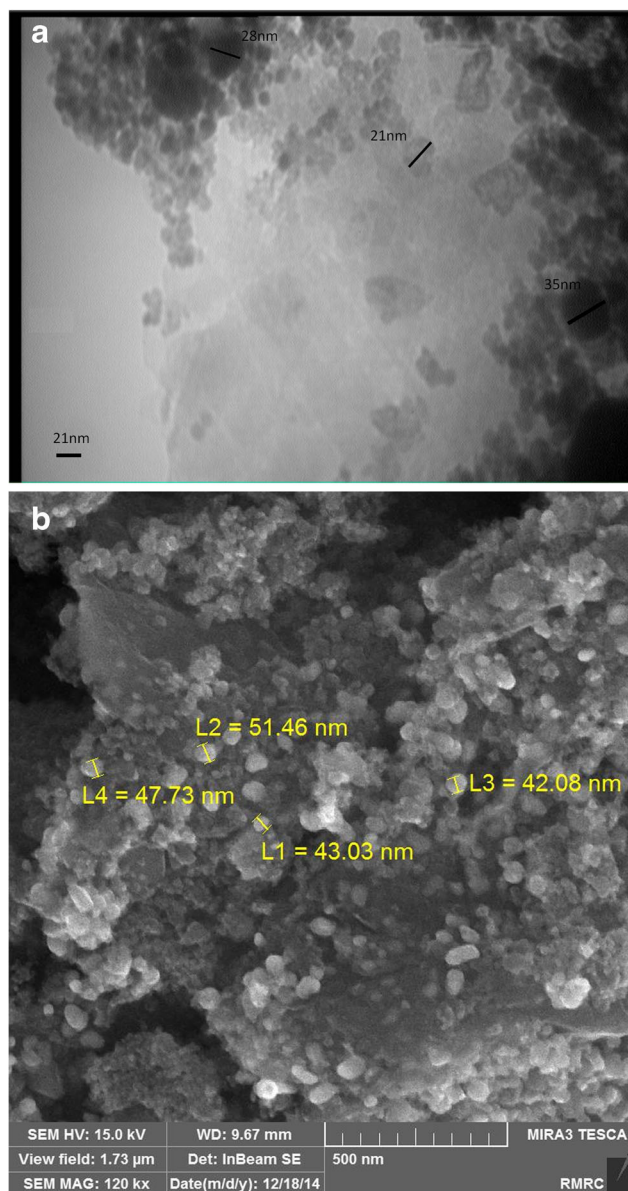
### Choice of materials

Gold nanoparticles are known to be biocompatible and less toxic, and also chemically stable. The aurum atom of gold nanoparticles can cause  $\pi$ -interaction with the analytes through the  $\pi$ -conjugated system. Therefore, the gold coating of the substrate can lead to the high extraction efficiency for OCPs. Also, graphene has remarkable properties such as huge surface area (with a calculated value of 2630 m<sup>2</sup> g<sup>-1</sup>), good chemical stability, and graphitized basal plane structure, which allow it to have strong  $\pi$ -interactions with the aromatic compounds [29]. Graphene tend to agglomerate and causes a great loss of effective surface area and consequently a lower adsorption capacity. Oxygen containing groups on GO surface can interact with Fe<sub>3</sub>O<sub>4</sub> and result in reduced graphene oxide. RGO can act as a substrate for  $\pi$ -interactions with OCPs. SPE with magnetic nanoparticles causes simple extraction due to the magnetic properties of the sorbent. Sorbent is easily separated from the solution by an external magnetic field. The presence of Fe<sub>3</sub>O<sub>4</sub> NPs on the GO surface may reduce its effective adsorption area and cause lower adsorption capacity for the sorbent due to the occupation of some of the active sites on the GO sheets by the Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The gold nanoparticles can compensate this reduction. Synergic effect of Au helped to extraction of OCPs due to  $\pi$ -interaction of gold and RGO with the analytes.

The extraction efficiencies of RGO/Fe<sub>3</sub>O<sub>4</sub> and RGO/Fe<sub>3</sub>O<sub>4</sub>@Au were compared for the OCPs in the same extraction conditions ( $n = 3$ ) include: 10 mL sample volume, 20 mg sorbent, 30 and 10 min extraction and desorption times, respectively, and 3 mL acetonitrile as eluent solvent which was finally concentrated to 0.5 mL. As the results shown in Fig. 1, RGO/Fe<sub>3</sub>O<sub>4</sub>@Au sorbent showed the higher extraction efficiency than RGO/Fe<sub>3</sub>O<sub>4</sub>.

### Characterization of RGO/Fe<sub>3</sub>O<sub>4</sub>@Au

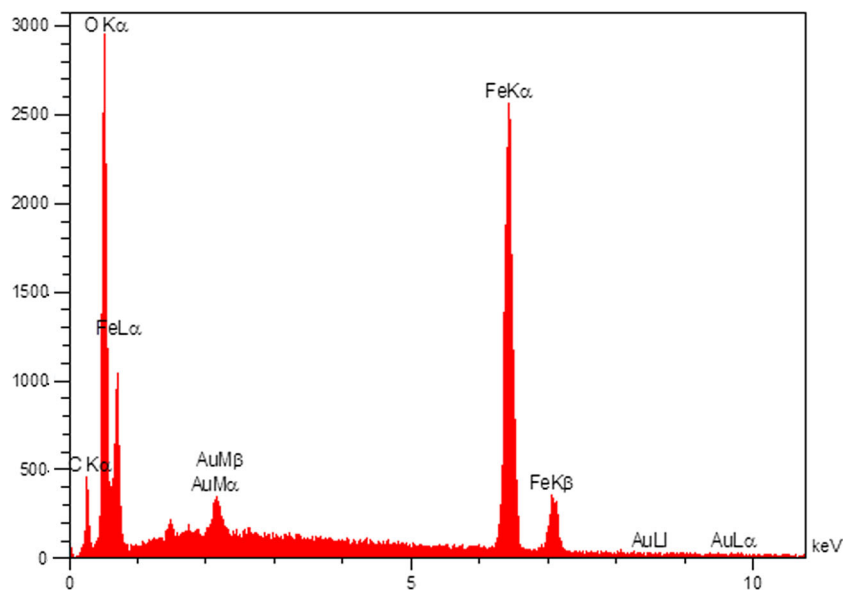
Figure 2 illustrated the FT-IR spectra of GO, RGO/Fe<sub>3</sub>O<sub>4</sub> and RGO/Fe<sub>3</sub>O<sub>4</sub>@Au. The spectra of the sorbent showed the O-H stretching vibration at 3457.2 cm<sup>-1</sup>. The peaks at 1174.8 cm<sup>-1</sup>



**Fig. 3** TEM image of reduced graphene/Fe<sub>3</sub>O<sub>4</sub>@Au at magnification of 100 (a) and SEM images of reduced graphene/Fe<sub>3</sub>O<sub>4</sub>@Au (b)



**Fig. 4** Energy-dispersive X-ray spectrum of reduced graphene/Fe<sub>3</sub>O<sub>4</sub>@Au



and 1031.2  $\text{cm}^{-1}$  can be attributed to the C-O stretching vibration. The C = C stretching vibration peak at 1622.0  $\text{cm}^{-1}$ , and Fe-O stretching vibration peak at 630.3  $\text{cm}^{-1}$  [30] was observed in the Fig. 2b and Fig. 2c. Moreover, comparison of the spectra of a, b and c in Fig. 2 shows a dramatic decrease in intensity of the adsorption peaks of oxygen containing functional groups, which indicates GO was partially reduced after magnetization by Fe<sub>3</sub>O<sub>4</sub>.

The morphology of RGO/Fe<sub>3</sub>O<sub>4</sub>@Au was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Figure 3 shows TEM and SEM images of RGO/Fe<sub>3</sub>O<sub>4</sub>@Au. Although the total structure is particulate, some aggregates can also be seen in SEM and TEM images. The size estimations from the SEM image showed that the mean diameter of particles were about 50 ( $\pm 10$ ) nm. As shown in Fig. 3a the prepared sorbent has the diameters in the range of 20–60 nm.

The EDX spectrum of the sorbent, shown in Fig. 4, indicates that Au nanoparticles anchored successfully onto the RGO/Fe<sub>3</sub>O<sub>4</sub> particles. The EDX analyzes were also performed for three batches of the product and the standard deviations of its elemental composition were as  $\pm 0.2$ ,  $\pm 1.0$  and  $\pm 0.8$  for Au, Fe and C, respectively. It shows the good reproducibility of the synthesis material from batch to batch.

### Optimization of the MSPE conditions

The effect of sample volume was examined in the range of 10–50 mL. The extraction conditions were as: 10 mg sorbent, 30 and 10 min extraction and desorption times, respectively, and 3 mL acetonitrile as eluent solvent which was finally concentrated to 0.5 mL. The concentration of OCPs was 100  $\mu\text{g L}^{-1}$  in working solution. As the results shown in the Figure S1a (Electronic Supplementary Material), high extraction recovery was observed in sample volume of 10 mL, and after that the extraction recoveries were reduced slowly. Therefore, 10 mL was selected for the subsequent experiments.

Different amounts of RGO/Fe<sub>3</sub>O<sub>4</sub>@Au ranging from 10 to 40 mg were exposed to 10 mL solution of OCPs. The extraction conditions include: 10 mL of sample (100  $\mu\text{g L}^{-1}$ ), 30 and 10 min extraction and desorption times, respectively, and 3 mL of acetonitrile as eluent solvent which was finally concentrated to 0.5 mL. The highest recoveries were obtained at 20 mg sorbent for all of the analytes (Online Resource 1b).

The influence of eluent volume was studied in the range of 0.1–0.5 mL. The extraction conditions include: 10 mL sample solution, 20 mg sorbent, and 30 and 10 min for extraction and

**Table 1** Figures of merit of MSPE-GC- $\mu$ ECD method for determination of OCPs

Analyte	Linearity ( $\mu\text{g L}^{-1}$ )	R <sup>2</sup>	LOD ( $\text{ng L}^{-1}$ )	LOQ ( $\text{ng L}^{-1}$ )	RSD ( $n = 3$ )	PF
Heptachlor	0.05–500	0.996	1.6	5.2	6.7	32
Aldrin	0.1–500	0.998	0.8	2.8	5.7	38
p,p' DDE	0.05–100	0.991	0.4	1.3	3.3	40
Dieldrin	0.05–100	0.994	2.4	7.9	2.2	40
p,p' DDD	0.05–100	0.994	2.7	8.9	1.7	39
p,p' DDT	0.1–500	0.999	4.1	13.6	7.3	38

desorption times, respectively. It was found that the highest extraction efficiency was obtained at 0.1 mL eluent solvent for most of the compounds (Online Resource 1c), but because of the practical problem of using this volume, 250  $\mu\text{L}$  was used for the subsequent procedures.

Desorption times were also studied in the range of 2–15 min. The extraction conditions include: 10 mL sample solution, 20 mg sorbent, 30 min extraction time, and 250  $\mu\text{L}$  acetonitrile as eluent. As can be seen in Figure S1d, 2 min was enough to elute the OCPs from the sorbent.

The extraction times were studied in the range of 2–30 min. The extraction conditions include: 10 mL sample solution, 20 mg sorbent, 2 min desorption time, and 250  $\mu\text{L}$  acetonitrile as eluent. As shown in Figure S1e, the extraction recovery increased to the highest level at 10 min.

To investigate the salt effect on the extraction recovery, different amounts of NaCl in the concentration range of 0–30 % (w/v) were added into the sample solutions. The extraction conditions include: 10 mL sample solution (100  $\mu\text{g L}^{-1}$ ), 20 mg sorbent, 2 and 10 min desorption and extraction times, respectively, and 250  $\mu\text{L}$  acetonitrile as eluent. The highest extraction recovery was obtained by adding 5 % NaCl into the sample for most of the compounds. According to the results (Online Resource 1f), the addition of salt would decrease the solubility of OCPs in the aqueous phase and increase the hydrophobic interaction between the OCPs and the extraction phase, therefore salt addition increase the efficiency of extraction (salting-out). On the other hand, more addition of salt decreased the extraction recoveries due to weaken of interaction between OCPs and G/Fe<sub>3</sub>O<sub>4</sub>@Au (salting-in).

### Reusability

To investigate the reusability of RGO/Fe<sub>3</sub>O<sub>4</sub>@Au, the sorbent was washed with 2 mL acetonitrile and then reused for next extraction under the optimized condition. The adsorption-desorption cycles were repeated seven times without any significant loss of the extraction efficiency.

### Method validation

The figures of merit of the introduced method including linearity, limit of detections (LODs), limit of quantitations (LOQs), relative standard deviations (RSDs) and preconcentration factors (PFs) were studied for the extraction of OCPs (Table 1). The analytes exhibited good linearities in the range of 0.05–500  $\mu\text{g L}^{-1}$  with the proper correlation coefficients ( $R^2$ ) from 0.991 to 0.999. The LODs and LOQs were in the range of 0.4–4.1 and 1.3–13.6  $\text{ng L}^{-1}$ , respectively. Preconcentration factors (PFs) were calculated based on the concentration ratio of the

**Table 2** Comparison of the introduced method with other reported extraction techniques used for determination of OCPs

Method	detection	LOD ( $\text{ng L}^{-1}$ )	RSD (%)	Ref
HS-SPME <sup>a</sup>	GC-ECD	50–97	3–8	[31]
DI-SPME <sup>b</sup>	GC-MS	-	<20	[32]
DLLME <sup>c</sup>	GC-ECD	10–100	5.8–8.8	[33]
D- $\mu$ -SPE <sup>f</sup>	GC-ECD	7.4–46.8	-	[34]
MSPE	GC- $\mu$ ECD	0.4–4.1	1.7–7.3	This work

<sup>a</sup> Head space solid phase micro extraction

<sup>b</sup> Direct immersion solid phase micro extraction

<sup>c</sup> Stir bar sorptive extraction

<sup>d</sup> Direct immersion single drop micro extraction

<sup>e</sup> Dispersive liquid-liquid micro extraction

<sup>f</sup> Dispersive micro solid phase extraction

analytes in the extraction phase that was injected ( $C_{\text{inj}}$ ) and that in the sample solution ( $C_s$ ):

$$\text{PF} = C_{\text{inj}} / C_s$$

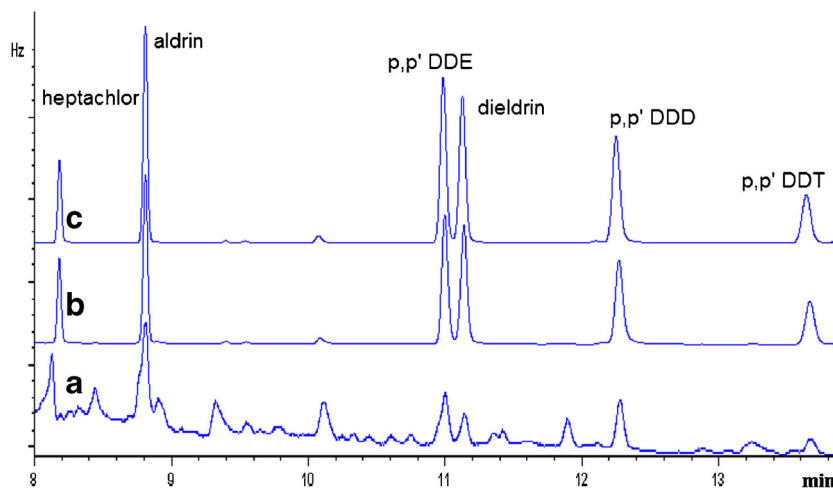
The PFs of the analytes were among 32–40, while the maximum theoretical PF value can be 40.

Table 2 compares the performance data of the introduced method and other methods reported in the literatures for analysis of the OCPs. The results show that the LODs and RSDs of the present method are better or comparable with the other works.

**Table 3** The recoveries of OCPs in sea water sample using the introduced method

analyte	Caspian sea		
	Add ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)
Heptachlor	0	N.D	-
	5.0	5.7	114
	50	46.6	93
Aldrin	0	2.9	-
	5.0	7.0	83
	50	45.7	86
p,p' DDE	0	1.3	-
	5.0	5.8	89
	50	45.6	89
Dieldrin	0	1.5	-
	5.0	6.4	97
	50	50.5	98
p,p' DDD	0	0.7	-
	5.0	6.3	113
	50	54.7	108
p,p' DDT	0	3.7	-
	5.0	7.8	81
	50	36.4	69

**Fig. 5** GC- $\mu$ ECD chromatograms of sea water samples after magnetic solid-phase extraction: non-spiked (a) and spiked water samples at  $5 \mu\text{g L}^{-1}$  (b) and  $50 \mu\text{g L}^{-1}$  (c)



### Analysis of real sample

To evaluate the performance of the method in real sample, it was applied for analyzing of the OCPs in sea water sample, collected from Caspian Sea. The detected concentration of the analytes were 2.89, 1.31, 1.55, 0.68,  $3.75 \mu\text{g L}^{-1}$  for aldrin, p, p' DDE, dieldrin, p, p' DDD, p, p' DDT, respectively. Heptachlor was not detected in the real sample. The recoveries for the spiked samples were ranged from 69 % to 114 % (Table 3). The chromatograms of the non-spiked and spiked seawater samples at two concentration levels ( $5$  and  $50 \mu\text{g L}^{-1}$ ) were shown in Fig. 5.

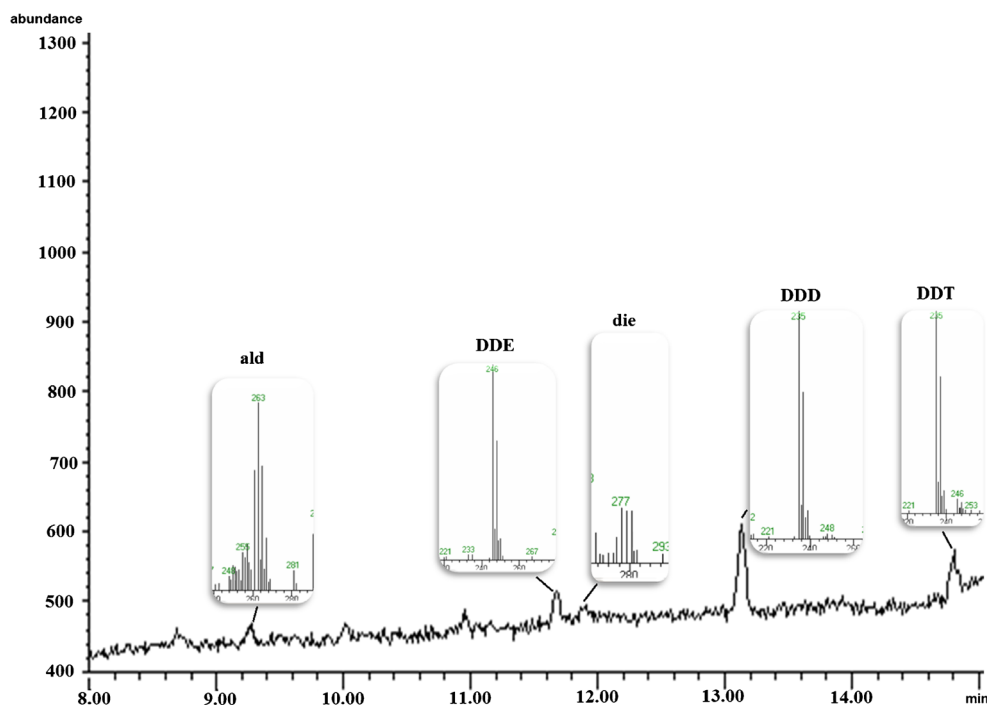
To confirm the gas chromatographic results in the real sample, GC-MS analysis was also performed for the non-spiked sample. As shown in Fig. 6, the analytes have been attended in

real sample and the result confirms the presence of OCPs in the real sample.

### Conclusion

The introduced sorbent exhibited excellent extraction efficiency for the OCPs, and it is expected that to have the potential to use as MSPE sorbent for other organic and inorganic analytes, especially for aromatic compounds. The use of Au showed considerable improvement in the adsorption and led to producing an adsorbent with the high extraction efficiency due to its  $\pi$ - interaction with the analytes and its high surface area. The introduced method showed good accuracy for determining OCPs in the environmental water samples. It was

**Fig. 6** Total ion current of non-spiked sea water sample and the mass spectra of the detected analytes



compatible with the environment, because of the low organic solvent consumption. It was also a quick, easy and sensitive method for determination of the OCPs. Low reusability, stability, selectivity are among the disadvantages of the introduced sorbent that functionalization of the composite material may overcome these limitations.

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