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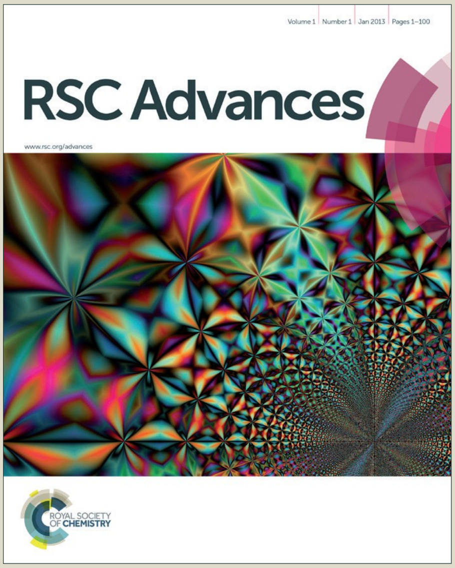

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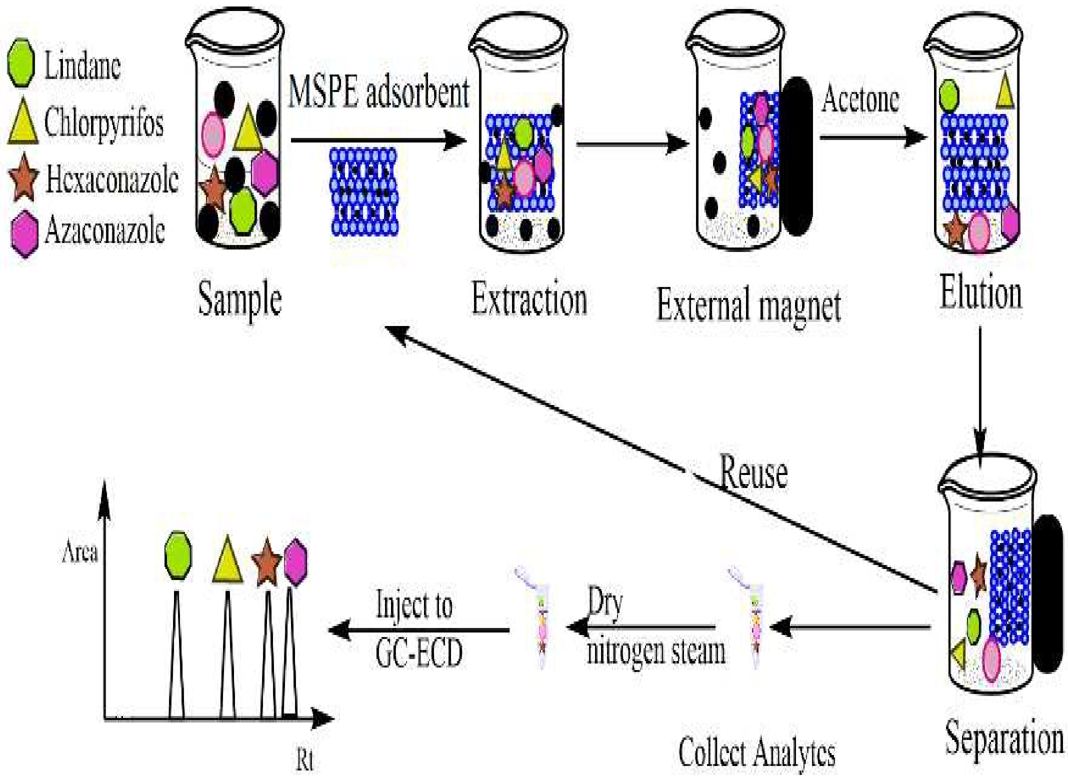
GRAPHICAL ABSTRACT



Dispersive graphene-based silica coated magnetic nanoparticles as new adsorbent for preconcentration of chlorinated pesticides from environmental water

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Abstract

The present study describes the synthesis, characterization and application of new graphene-based silica coated magnetic nanoparticles (Fe_3O_4@SiO_2-G) for the simultaneous preconcentration of four chlorinated pesticides namely lindane, chlorpyrifos, hexaconazole and azaconazole from contaminated water. The newly synthesised adsorbent was characterized using FT-IR spectroscopy, field emission scanning electron microscopy (FESEM), energy dispersive spectroscopy (EDS) and X-ray diffractometer (XRD). Chlorinated pesticides extraction efficiency of the Fe_3O_4@SiO_2-G was evaluated through magnetic solid phase extraction (MSPE) using gas chromatography with micro electron capture detector (GC-μECD). Experimental parameters, i.e., desorption solvent, solvent volume, extraction time, desorption time, sample volume, adsorbent dosage and solution pH were optimized. Compared to commercial C18 sorbent and Fe_3O_4@SiO_2, the newly synthesized Fe_3O_4@SiO_2-G adsorbent showed linear response (1-100 pg mL^{-1}), low limits of detection (0.12-0.28 pg mL^{-1}) and high adsorption capacity (13.04-18.69 mg g^{-1}) with coefficient of determination (R^2) of 0.999. Environmental water samples were used to assess the field applicability of the adsorbents. Excellent percent recovery (80.8-106.3%) was achieved for Fe_3O_4@SiO_2-G at pH 6.5. Results showed that the newly synthesized Fe_3O_4@SiO_2-G is an efficient and highly potential adsorbent for the preconcentration of selected chlorinated pesticides from aqueous media.

Keywords: Graphene; Fe_3O_4@SiO_2-graphene nanocomposite; chlorinated pesticides, preconcentration; magnetic solid phase extraction.

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1. Introduction

Since, from the origin of pesticides to this day, a remarkable increase in the usage of pesticides has been observed. Recent literature surveys indicated that per annum worldwide consumption of pesticides have exceeded to 2.5 million pound.[1] Approximately more than 28% contribution of chlorinated pesticide in the total pesticide consumption makes them representative and largest class of pesticides. Generally chlorinated pesticides are used as triazine herbicides, fungicides and insecticides for crop protection.[2] The massive use of chlorinated pesticides is one of the most imperative issues of the modern era because due to the widespread usage these pesticides can be easily mixed to the natural stream.[1,3] Particularly water contamination as a result of chlorinated pesticides is becoming hottest issue for the environmental researchers. From environmental point of view the mixing of chlorinated pesticides as well as their degraded products into the natural streams is of great concern.[4] Because pesticides can be easily transferred to drinking water and becomes harmful to human health.[5] Toxicity of chlorinated pesticides has been comprehensively reviewed; literature survey showed that constant exposure to chlorinated pesticides can cause several life-threatening ailments, such as cancer, disorders of the reproductive and endocrine system.[6-8] European Union has declared the safe concentration levels for pesticides is 0.1 ng mL^{-1}, while a very high concentration of pesticides (i.e., 0.43 mg L^{-1}) has been reported.[9] Consequently, due the exceeded limit as well as well-known toxicity of chlorinated pesticides and their degraded products, the precise determination and extraction is extremely necessary.[10]

Several techniques, including liquid-liquid extraction (LLE), liquid phase microextraction (LPME), stir bar sorptive extraction (SBSE), solid phase micro extraction (SPME), dispersive solid phase extraction (DSPE) and solid phase extraction (SPE), have been applied to remediate the pesticides and their degraded products from the aqueous environment.[11,12] Comparatively, SPE due to its simplicity, significant recovery, short extraction time, high enrichment factor and low cost is renowned as an advantageous and authentic method.[13] A variety of materials such as electrospun modified silica,[14] inorganic oxide nanoparticles/polyethylene,[15] C18,[16] TEOS-MTMOS,[12] multi wall carbon nanotube,[17] chitosan/ polypyrrole[18] and graphene have been used as extraction adsorbent.[19] But due to the low adsorption efficiency and reusability, the use of conventional materials is limited. Consequently, exploitation of innovative highly selective pesticide sorbents which can be easily regenerated as well as effectively use in aqueous media has currently become a focus of intensive research.[20-22] In this regard graphene due to honeycomb-like structure deserves particular attention. Additionally, high surface area, significant adsorption capacity, variety of benzene rings and especially rich π-π electron arrangement makes the graphene as a suitable extractant for the extraction of benzene based pesticides.[23,24]

Literature survey reveals that graphene-based materials are mostly use for pesticides decontamination.[25-27] However, graphene-based extraction reagents suffer from some drawbacks such as hydrophobicity as well as dispersive nature in aqueous media which makes the extraction process tedious and time consuming. These drawbacks can be abridged through the functionalization of graphene with willful molecular frameworks. In this respect, magnetic Fe_3O_4 nanoparticles provided important avenues to prepare new, stable and efficient extraction reagents[28,29] as well as green sample preparation.[30] Since, SiO_2 is cheap, environment friendly, chemically stable and highly dispersive in liquid due to it rich O-H groups. So, generally Fe_3O_4 are coated with different silane derivatives via sol-gel method to increase the surface area porosity and effective binding sites.[31,32] Thus, in this study we reported the synthesis, characterization and application of graphene-based silica-coated magnetic nanoparticles (Fe_3O_4@SiO_2-G) for the preconcentration of four chlorinated pesticides namely lindane, chlorpyrifos, hexaconazole and azaconazole from contaminated water. The chlorinated pesticides concentration was determined by GC-μECD.

1. Experimental

2.1 Material

Lindane, chlorpyrifos, hexaconazole, azaconazole and propazine (internal standard) were from Riedel-de Haen (Hanover, Germany). Analytical grade reagents/chemicals were used. Graphite powder and tetraethoxysilane (TEOS) were purchased from Sigma Aldrich (St. Louis, MO, USA). Sulphuric acid (98%), nitric acid (65%), hydrochloric acid (37%), ethanol (97%) and HPLC grade methanol were from QReC (Selangor, Malaysia).

2.2 Instrument

FT−IR spectra (4000-400 cm^{-1}) were recorded on a 1600 series Perkin-Elmer FTIR Spectrometer (MA, USA) as KBr pellets. A D8-Advance X-ray diffractometer from Bruker (GmbH. Karlsruhe, Germany) was used for crystal analysis with Cu Kα radiation (λ = 1.54060 Å), high quality mode and 40 kV voltage. The size, morphology, structure and composition of the newly magnetic materials were observed using a Carl Zeiss Model Supra 35-VP FESEM (Oberkochen, Germany) operated at 10.0 kV, magnification 50000× and a working distance (WD) of 6.0 mm. Agilent A7600 gas chromatography equipped with a micro electron capture detector (GC-μECD) (Santa Clara, CA, USA) was used for the selected chlorinated pesticides analysis.

2.3 Gas chromatography conditions

GC-μECD with HP-5MS column (5% Phenyl Methyl Siloxane 325°C: 30 m × 250 μm × 0.25 μm) was used for the identification of the selected chlorinated pesticides in the water samples. The optimum GC-μECD conditions are as follows: Helium was used as back inlet carrier gas at a flow rate of 2.5 mL min^{-1} and nitrogen was used a back detector make up gas at a flow rate of 5 mL min^{-1}. The back inlet port and detector temperature was set at 280°C (pressure set 25 psi) and 300°C, respectively. Gas chromatography temperature profile was set at 70-280°C, starting at 70°C (held for 1 min) ramp at 50°C min^{-1} to 190°C (held for 1 min) and ramp at 30°C min^{-1} to 280°C (held for 2 min). 1 μL of the extracted analytes in methanol was injected manually into the injection port under splitless mode. Triplicate injections were performed for each extract and the average peak area ratio reading was taken

2.4 Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 magnetic nanoparticles (MNPs) (Fig.1A) were prepared via the modification of previously reported procedure.[33] 0.5 g of $(NH_4)_2Fe(SO_4)_2·6H_2O$ and 1 g $FeCl_3·6H_2O$ were dissolved in 30 mL of deionized water and stirred vigorously for 5 min at $50^{\circ}C$. Following the drop wise addition of 5 mL of ammonia solution (32%), reaction mixture was further stirred at room temperature for 5 h. The resulting black Fe_3O_4 nanoparticles were collected using external magnet and washed with excess of deionized water and dried under vacuum at $80^{\circ}C$ for 24 h.

2.5 Synthesis of $Fe_3O_4@SiO_2$

Tetraethyl orthosilicate (TEOS) coated magnetic nanoparticles (Fig. 1B) were prepared by the modification of Stöber method.[34] SiO_2 coating of the Fe_3O_4 MNPs has been shown to enhance the lifetime as well as binding sites of the MNPs.[31,32] 0.5 g of the freshly prepared Fe_3O_4 were dispersed in 100 mL of water/ethanol solution (1:1) then 0.5 mL TEOS was added into the solution. Following the addition of 5 mL ammonia solution (25%) the reaction mixture was stirred for 1 h and then left at room temperature for 20 h. Finally, the resultant slightly darker brown $Fe_3O_4@SiO_2$ nanoparticles were collected and washed with deionized water and ethanol. The $Fe_3O_4@SiO_2$ was then dried under vacuum at 80°C for 20 h.

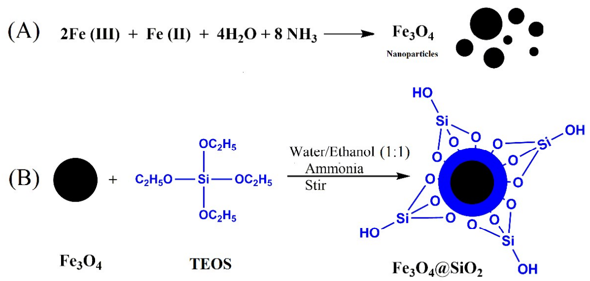

Fig. 1 Schematic synthesis of (A) magnetic Fe_3O_4 nanoparticles and (B) silica-coated magnetic nanoparticles

2.6 Preparation of Graphene Oxide

2 g of natural graphite was soaked in 10 mL of concentrated HCl for 48 h. The mixture was then filtered and the filtrate was washed with excess of deionized water and dried under vacuum at 80°C for 24 h. The dried natural graphite was suspended in a mixture of 120 mL of concentrated H_2SO_4/HNO_3 (2:1) and stirred at room temperature for 1 h. Potassium permanganate (3 g) was then added gradually into the reaction mixture and was further stirred at room temperature for 24 h. Finally, yellow-coloured graphene oxide (GO) was obtained by

adding ice (500 g) and H_2O_2 (3 mL). The resultant product was washed with excess of deionized water and then dried at 80°C for 24 h under vacuum.

2.7 Synthesis of Fe_3O_4@SiO_2-Graphene

Fe_3O_4@SiO_2-Graphene MNPs (Fig. 2) were prepared as follows; 10 mg of freshly prepared Fe_3O_4@SiO_2 were dispersed into the 50 mL of graphene oxide (GO) solution (10 mg mL^{-1}) followed by the addition of 2 mL of ammonia solution (32%) and 5 mL of hydrazine hydrate. The reaction mixture was stirred at room temperature for 48 h. The resulting Fe_3O_4@SiO_2-Graphene MNPs were separated by external magnate and washed with excess deionized water; then dried at 80°C for 24 h.

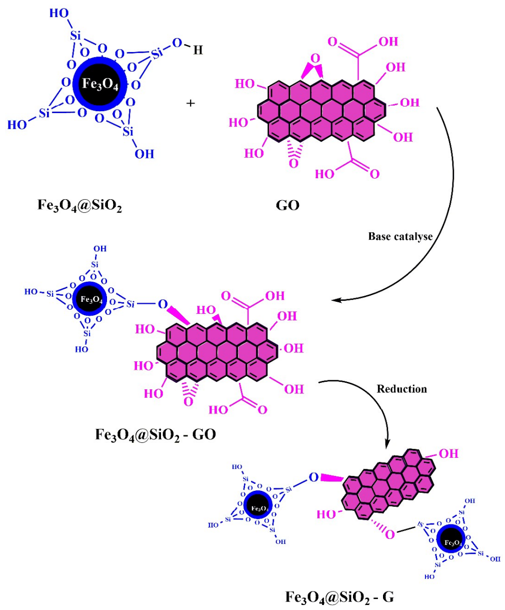

Fig. 2 Schematic mechanism of preparation of graphene-based magnetic nanoparticles

2.8 Water sample preparation

Four environmental water samples namely tap, river, lake and sea were used to assess the field application of synthesized Fe_3O_4@SiO_2-Graphene. Tap water was obtained from the laboratory, while river and lake water samples were taken from Melana River and UTM Lake, Skudai, respectively. Sea water sample was taken from Danga Bay, Johor Bahru. Tap water was used directly without further treatment. River, lake and sea water samples were filtered using Whatman cellulose filter paper (125 mm diameter, 11 µm pore size and 180 µm thickness) for the removal of debris.

2.9 Extraction procedures for selected chlorinated pesticides

2.9.1 Optimization of MSPE parameters

Different parameters i.e., types of desorption solvent, solvent volume, adsorption time, desorption time, sample volume, adsorbent dosage and solution pH were optimized during the MSPE. Initially, 10 mL of sample volume, 10 mg of adsorbent and 20 min extraction time were used for extraction of the selected chlorinated pesticides. The chlorinated pesticides were eluted using 1 mL of different types of solvents.

2.9.2 Magnetic solid phase extraction

Fig. 3 shows the schematic diagram of MSPE process for the extraction of selected chlorinated pesticides using synthesized Fe_3O_4@SiO_2-G MNPs. The experiments were performed in Erlenmeyer flasks (100 mL) which contain 60 mg of the adsorbent and 50 mL of 1 ng mL^{-1} solution of each chlorinated pesticide or adsorbed solution. For the equilibrium flasks were shakened on an orbital shaker at a constant speed of 250 rpm at 25°C for 5 min. The adsorbent was then separated using an external magnet and trapped analytes were desorbed using 3 mL of acetone. The eluted solution was evaporated by blowing a gentle stream of nitrogen gas and reconstituted with 50 µL of propazine (100 ng mL^{-1} in methanol) as an internal standard (IS). Finally, 1 µL of reconstitute solution was injected into GC-µECD to determine the extracted lindane, chlorpyrifos, hexaconazole and azaconazole. Triplicate injections were performed for each extract and average peak area ratio reading was taken

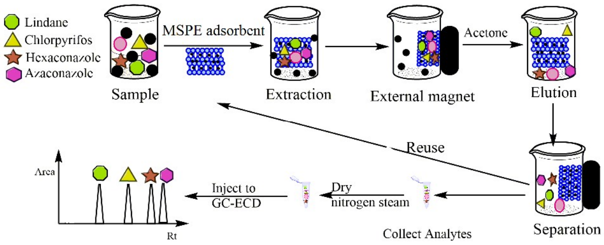

Fig. 3 Schematic representation of graphene-based MSPE procedure

2.9.3 C18-SPE procedure

Commercial C18-SPE cartridge was optimized with important extraction parameters such as type of solvent, volume of solvent, sample volume and flow rate. Acetone, acetonitrile, methanol, ethyl acetate and *n*-hexane were used to optimize the solvents effect on C18 SPE. Comparatively, high extraction efficiency was achieved using acetonitrile (0.5 mL to 5 mL). On the basis of results, 2 mL of acetonitrile was selected as the optimized solvent volume. In order to improve the preconcentration factor, sample volume was also optimized (1 mL to 50 mL). Maximum extraction efficiency was obtained with 10 mL of sample volume and thus selected as optimized sample volume. Best result was achieved at 0.5 mL min^{-1} flow rate.

2.10 Adsorption capacity

At optimized conditions adsorbent capacity (q_e) was investigated for residual chlorinated pesticides in water samples. The residual concentration of chlorinated pesticides was analyzed using GC-µECD by reconstituting the analyte with 100 µL methanol as described previously.[35] The adsorption capacity was calculated using equation (1) as follows:

$$q_e = \frac{V}{m}(C_0 - C_e) \qquad (1)$$

where q_e is adsorption capacity (mg g^{-1}), V is initial volume of the sample (L) before pretreatment, m is mass of applied adsorbent (g) for extraction, C_0 is initial concentration (mg L^{-1}) and C_e is residual concentration (mg L^{-1}) of analytes in the solution produced after extraction.

3. Result and Discussion

3.1 Characterization

3.1.1 FT-IR Spectra

The synthesis of $Fe_3O_4@SiO_2$, functionalization of graphene and immobilization of functionalized graphene onto the $Fe_3O_4@SiO_2$ was confirmed by FT-IR spectral analysis (Fig. 4A-C). Since natural graphite do not contain any functional group. But following the functionalization process resultant GO (Fig. 4A) shows some additional bands at 3372, 1720, 1625, 1436, 1168 and 1050 cm^{-1} for of O-H, C=O, C=C, C-C, epoxy groups and C-O group stretching, respectively.[21] The appearance of sharp bands (Fig. 4B) at 582and 1100 cm^{-1} corresponds to Fe-O and Si-O symmetric stretching, respectively.[35] The formation of

Fe_3O_4@SiO_2-G MNPs was confirmed by the appearance as well as disappearance of characteristic bands. Since IR spectra of GO (Fig. 4A) do not show Si-O stretching band, while following the immobilization with Fe_3O_4@SiO_2 the resultant material Fe_3O_4@SiO_2-G MNPs shows a band at 1100 cm^{-1}. Additionally, during the immobilization Si-O group intensity also reduced and disappearance of characteristic band at 1720 and 1168 cm^{-1} for C=O and epoxy groups (Fig. 4C) respectively also offer proof for the formation of Fe_3O_4@SiO_2-G MNPs. Consequently appearance and disappearance of some characteristic peaks is a qualitative evidence which confirms the immobilization of GO onto Fe_3O_4@SiO_2 as well as formation of Fe_3O_4@SiO_2-G MNPs.

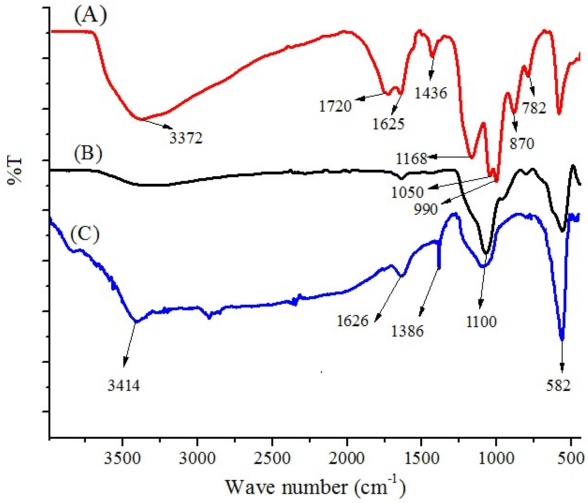

Fig. 4 FT-IR spectra of (A) GO, (B) Fe_3O_4@SiO_2 and (C) Graphene-based magnetic nanocomposite

3.1.2 Field emission scanning microscopy

The morphology of the newly synthesized magnetic graphene-based adsorbent (Fe_3O_4@SiO_2-G) was analyzed using field emission scanning microscopy (FESEM). White cloud-like appearance (Fig. 5A) clearly shows that nanosize visible graphene sheets have been successfully immobilized with silica coated MNPs of $Fe_3O_4@SiO_2$. Furthermore, in order to examine the purity and elemental composition of silica coated MNPs immobilized material ($Fe_3O_4@SiO_2$-G), FESEM was coupled with energy dispersive spectroscopy (EDS). The EDS results (Fig. 5B) showed 50%, 17.91% and 5.50%, and of C, Fe and Si respectively, in the $Fe_3O_4@SiO_2$-G. As we know that graphene oxide does not contain Si and Fe, as well as $Fe_3O_4@SiO_2$ do not contain C. But after the immobilization of $Fe_3O_4@SiO_2$ onto the modified graphene oxide, presence of Si, Fe and C confirmed the successful immobilization.

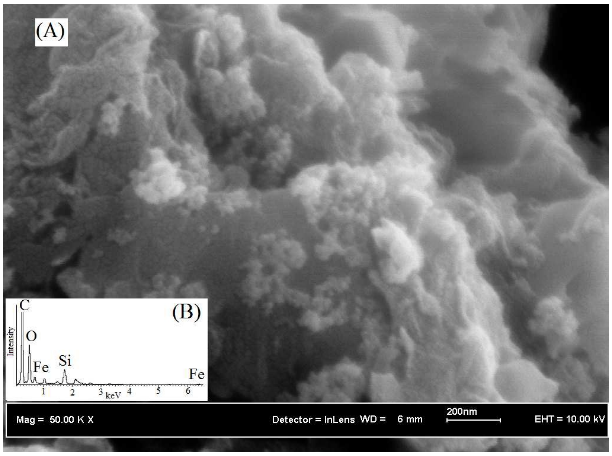

Fig. 5 (A) Micrograph image and (B) EDS spectra of the graphene-based silica MNPs

3.1.3 XRD

Fig. 6 shows the XRD signals of Fe_3O_4, $Fe_3O_4@SiO_2$, and $Fe_3O_4@SiO_2$-G. The Fe_3O_4 signals appeared as 2θ values of 30.14° (220), 35.51° (311), 43.15° (400), 53.44° (422), 57.09° (334), 62.68° (400) and 74.16° (533) . In Fig. 6B, the broad peak at 20.44° revealed that following the coating with SiO_2 the intensity of Fe_3O_4 has decreased. GO skeleton possess significantly high diffraction signals at $2\theta = 10.3°$ (001) and a weak one at 43.3° (101).[28, 36, 37]

The disappearance of high diffraction signal for GO and appearance of a broad band signal at 26.1° in XRD spectra (Fig. 6C) may be attributed to the successful conversion of GO into graphene sheet through reduction process in basic solution i.e., hydrazine hydrate and ammonia solution. The XRD results of the synthesized Fe_3O_4 MNPs completely matched by the library template pattern number 01-071-6336. Furthermore, the quite small size of Fe_3O_4 particles can be predicted by wider signals in XRD spectra.[38]

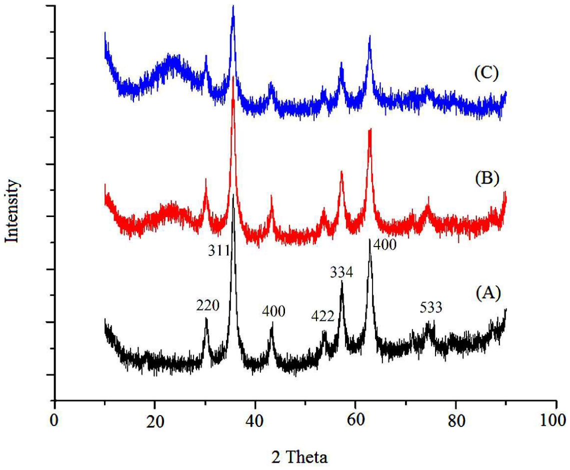

Fig. 6 XRD patterns of (A) Fe_3O_4 (B) $Fe_3O_4@SiO_2$ and (C) $Fe_3O_4@SiO_2$-G magnetic nanocomposite

3.2 Optimization of different parameters

The batch-wise MSPE study was carried out to evaluate the extraction efficiency of synthesized $Fe_3O_4@SiO_2$-G adsorbent for the selected chlorinated pesticides. Important parameters such as of desorption solvent, volume of solvent, extraction time, desorption time, sample volume and pH were optimized.

3.2.1 Types of desorption solvent

The effect of desorption solvent on MSPE performance have been investigated using seven organic solvents of different polarity. It is obvious from Fig. 7A that significant extraction efficiency was obtained with 3 mL acetone.

3.2.2 Extraction and desorption time

The extraction and desorption times are the key parameters for effective MSPE process. To optimize extraction time trials ranging from 1 to 90 min were used, highest peak area ratio was observed within 3 min. For desorption time, time settings from 1 to 5 min were studied. The peak area was significantly highest in 1 minute. Thus, 3 min and 1 min were selected as the extraction and desorption times, respectively.

3.2.3 Sample Volume

In order to obtain high enrichment factor the sample volume (5 to 80 mL) was investigated (Fig. 7B). By increasing the volume (5-50 mL), enrichment factor increased as well as the peak area ratio is also increased and it attains maximum at 50 mL of sample volume. Beyond the 50 mL of sample volume there is no significant change in the peak area, consequently 50 mL was chosen as the optimized sample volume for further analysis.

3.2.4 Adsorbent dosage

The effect of adsorbent dosage on the percent extraction of chlorinated pesticides was assessed by changing the mass of adsorbent ranging from 10 to 120 mg (Fig. 7C). Increasing the mass of adsorbent, increase the % extraction of the chlorinated pesticides The dosage study clarified that chlorinated pesticides extraction efficiency remarkably increased up to the 60 mg of adsorbent. There after increasing the mass of adsorbent did not produce significant improvement in % extraction. Consequently, all the experiments were performed with a fixed mass of adsorbent i.e., 60 mg.

3.2.5 Solution pH study

pH is also one of the key parameters and play an imperative role during the adsorption process. It affects the aqueous chemistry as well as the dissociation of functional groups on the active sites of the adsorbent. Consequently, effect of solution pH on the pesticides adsorption using the graphene-based magnetic adsorbent was examined at different pHs (i.e., 3.5, 5.0, 6.5, 8.0 and 10.0). It can be seen from Fig. 7D that the peak area of the isolated chlorinated pesticides in acidic condition was higher as compared to basic media. The high extraction of chlorinated pesticides in slightly acidic medium i.e., pH 6-7 can be explained on the basis of point zero charge (PZC) of graphene-based material. In acidic medium (pH 5.0 to 6.5) graphene- based adsorbent had a net positive surface charge.[39, 40] Results showed that by decreasing the solution pH, extraction increases and it attains maximum i.e., 88.5%, 92.9%, 100.9% and 96.9% for lindane, chlorpyrifos hexaconazole and azaconazole pesticide, respectively at pH 6.5. In this case the probable mechanism is surface complexation by means of surface association between the acidic hydroxyl ($^{+}OH_2$) groups of graphene-based adsorbent and anionic sites of chlorinated pesticides. While at low pH, decrease in extraction efficiency may be due to the repulsion between positive surface of adsorbent and positive ions on the chlorinated pesticides. On the other hand at higher pH the deprotonation of the phenolic hydroxyl groups of graphene moiety in the graphene-based adsorbent converts them into negative charged phenoxide ions. Following the deprotonation as well as due to the abundance of OH^{-} ions, extraction of chlorinated pesticides decreases. The dramatically decreased in % extraction of chlorinated pesticides at higher pH (pH 8) is due to the fact that pesticides undergo hydrolysis rather than adsorption.[41, 42]

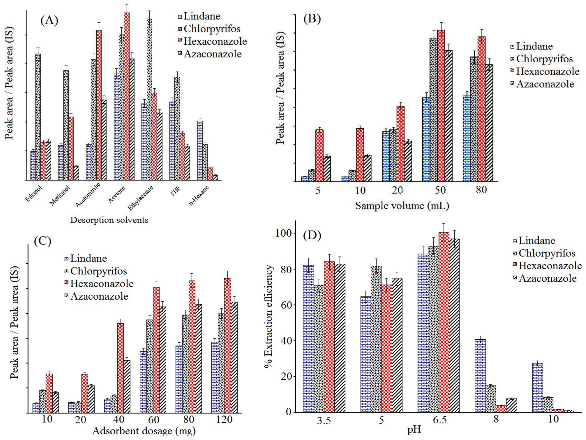

Fig. 7 Effect of (A) elution solvent, (B) sample volume, (C) adsorbent dosage and (D) solution pH on chlorinated pesticides extraction efficiency

3.3 Comparison of extraction performance

Comparative studies were performed in order to compare the extraction performance of the newly synthesized $Fe_3O_4@SiO_2$-G adsorbent with $Fe_3O_4@SiO_2$ and commercially available C18-SPE cartridge (100 mg) for the preconcentration of chlorinated pesticides. Fig. 8 shows that high sensitivity of C18 is only for the non-polar chlorpyrifos (Log $K_{O/W}$ 4.7) and hexaconazole (Log $K_{O/W}$ 3.6) since it only provides non-covalent hydrophobic interactions. Due to SiO_2 porosity and polar hydroxide groups, $Fe_3O_4@SiO_2$ shows slightly higher efficiency for moderately polar azaconazole (Log $K_{O/W}$ 2.7). While, the newly synthesised $Fe_3O_4@SiO_2$-G adsorbent showed significantly higher extraction efficiency for both the non-polar as well as moderately polar chlorinated pesticides namely chlorpyrifos, hexaconazole and azaconazole. The higher extraction efficiency of the newly synthesized $Fe_3O_4@SiO_2$-G for non-polar as well as moderately polar pesticides can be explained on the fact that the newly synthesized adsorbent contains benzene moiety which can form strong π-π interaction with the benzene ring of the selected chlorpyrifos, hexaconazole and azaconazole pesticides. Additionally, H-bonding interaction was also observed (Fig. 9) and lindane affinity can be explained by hydrophobic and electrostatic interaction.

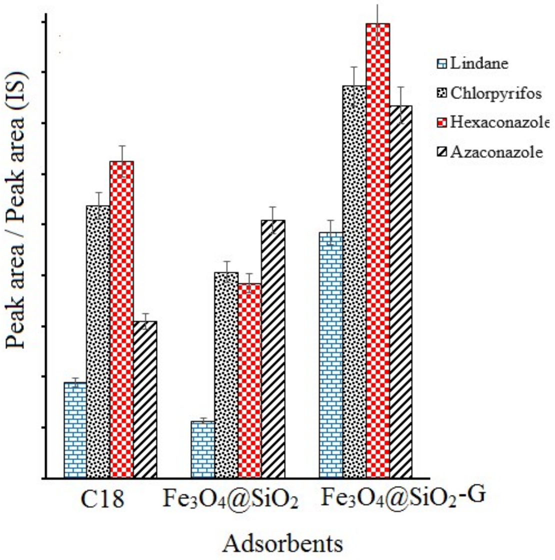

Fig. 8 Comparison of extraction performance (based on peak areas ratio) of three different sorbents for the chlorinated pesticides pre-concentration. Conditions for extractions: sample volume 10 mL, concentration of analytes 1 ng mL, EF 100, extraction time 5 min, desorption time 3 min and 3 mL acetonitrile as desorption solvent

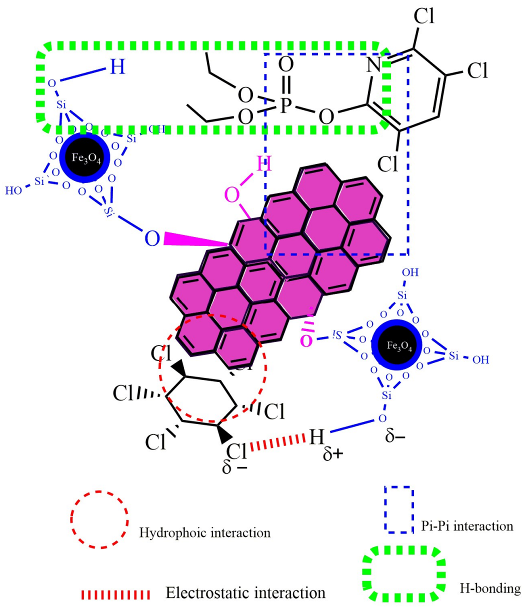

Fig. 9 Proposed mechanism for the adsorption of the chlorinated pesticides by $Fe_3O_4@SiO_2$-G

3.4 Adsorption study

Adsorption capacity (q_e) of the newly prepared $Fe_3O_4@SiO_2$, $Fe_3O_4@SiO_2$-G adsorbents and C18-SPE sorbent for chlorinated pesticides was calculated using Equation (1). Plot of q_e versus C_e (residual concentration) as shown in (Fig. 10A) illustrates that adsorption capacity of $Fe_3O_4@SiO_2$-G was increased by increasing the residual concentration until the adsorbent sites were saturated.

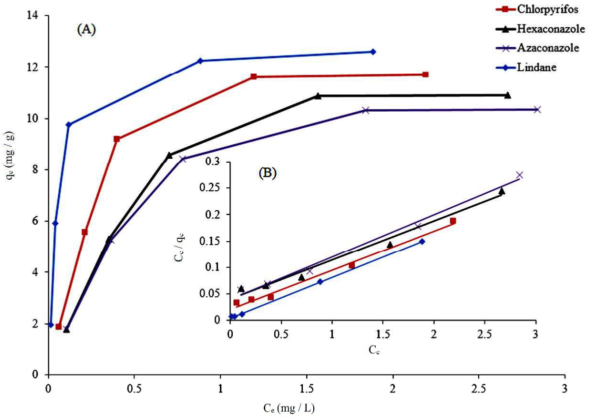

Fig. 10 (A) Experimental adsorption capacity of newly synthesized sorbent and (B) Langmuir linearity. Conditions: 50 mL sample in deionized water (0.1-7 µg mL^{-1}), extraction time 3 min, and adsorbent 60 mg

3.5 Adsorption isotherms

The correlation between the amounts of solute adsorbed per unit amount of the adsorbent and concentration of adsorbate in bulk solution at a given temperature under equilibrium conditions can be analyzed by using adsorption isotherms. The analysis of isotherm data plays a significant role in predicting the maximum adsorption capacity (q_m) of the adsorbent. Consequently, three well known isotherm model namely Langmuir, Freundlich and Temkin isotherm were tested in the following way:[43]

Langmuir: $$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{kq_m} \qquad (2)$$

Freundlich: $$Lnq_e = LnK_F + \left(\frac{1}{n}\right)LnC_e \qquad (3)$$

Temkin: $$q_e = BLnA + BLnC_e \qquad (4)$$

Where C_e is the residual concentration of pesticides in the solution (mg L^{-1}), q_e is the experimental adsorption capacity (mg g^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), k is Langmuir constant (L mg^{-1}), K_F [(mg/g)/(mg/g)$^{1/n}$] and n is the Freundlich isotherm constants. A is Temkin equilibrium constant (L g^{-1}) and B is the heat of sorption constant (J mol^{-1}).

Good linearity was obtained with Langmuir isotherm model (Fig. 10B). Thus, adsorption of the selected chlorinated pesticides were well fitted by Langmuir isotherm model as compared to Freundlich isotherm and Temkin model due to high value of coefficient of determination (R^2). The q_m values (Table 1) showed that the newly synthesized $Fe_3O_4@SiO_2$-G adsorbent possess high adsorption capacity (q_m) for the selected chlorinated pesticides. However, the $Fe_3O_4@SiO_2$-G provided 16× and 30× higher adsorption capacity as compared to the $Fe_3O_4@SiO_2$ and C18-SPE, respectively.

Table 1 Maximum adsorption capacity (q_m) for C18-SPE, $Fe_3O_4@SiO_2$ NPs and $Fe_3O_4@SiO_2$-G

Model	**Maximum adsorption capacity (q_m)**			
	Lindane	Chlorpyrifos	Hexaconazole	Azaconazole
C18	0.82	0.73	0.63	0.64
$Fe_3O_4@SiO_2$	1.58	1.82	2.1	1.18
$Fe_3O_4@SiO_2$-G	13.04	16.58	18.69	15.35

3.6 Method Validation

The analytical performance of the proposed magnetic graphene-based MSPE method was validated using different analytical parameters such as linearity, limit of detection (LOD), limit of quantification (LOQ), precision (RSD%), reusability and enrichment factor (EF). The linearity of the MSPE technique for chlorinated pesticide using $Fe_3O_4@SiO_2$-G, $Fe_3O_4@SiO_2$ and commercial SPE-C18 was examined at different concentration levels i.e., 0.001-0.1 ng mL^{-1}, 0.1-1 ng mL^{-1} and 0.5-10 ng mL^{-1}, respectively. Good linearity with high value of coefficient of determination (R^2) i.e., 0.9991-0.9998 were obtained for the selected chlorinated pesticides (Table 2). The final concentration was calculated using method calibration graph i.e., (A_x/A_{is}) versus (C_0/C_{is}), where A_x is peak area after extraction, A_{is} is peak area for internal standard, C_0 is initial concentration (ng mL^{-1}) and C_{is} is internal standard concentration (ng mL^{-1}). The LOD (S/N = 3) obtained for all pesticides were between 0.1 and 0.3 pg mL^{-1} ($n = 3$) with 1000× EF. Table 2 showed that LOD for $Fe_3O_4@SiO_2$-G is appreciably low as compared to the $Fe_3O_4@SiO_2$ and commercial C18-SPE. The LOD obtained for $Fe_3O_4@SiO_2$-G is below the MRL i.e. 100 pg mL^{-1} as set by US EPA or EU for each pesticide in drinking water.

The repeatability and reproducibility of the proposed MSPE method were investigated using intraday and interday precisions. Relative standard deviation (%RSD) was assessed for extraction of 1 ng mL^{-1} chlorinated pesticides followed by preconcentration thrice in a day (intraday) for five consecutive days (interday) (Table 3). The interday value looks little bit exceeded but ANOVA showed no significant difference between the whole analysis, since, p >

0.05 and $F_{experimental;} < F_{table}$ at 95% confidence level. Thus repeatability and reproducibility values for proposed MSPE method are acceptable.

Table 2 Statistical results of MSPE method, including limit of detection (LOD), limit of quantification (LOQ), linearity and enrichment factor (EF) using three different adsorbents

Validation	Sorbent	Analytes			
		Lindane	**Chlorpyrifos**	**Hexaconazole**	**Azaconazole**
Linearity (ng mL^{-1})	C18	0.5-5	0.5-5	0.5-5	0.5-5
	Fe_3O_4@SiO_2	0.1-1	0.1-1	0.1-1	0.1-1
	Fe_3O_4@SiO_2-G	0.001-0.1	0.001-0.1	0.001-0.1	0.001-0.1
***R*²**	C18	0.9996	0.9997	0.9999	0.9997
	Fe_3O_4@SiO_2	0.9998	0.9993	0.9994	0.9996
	Fe_3O_4@SiO_2-G	0.9997	0.9995	0.9998	0.9994
LOD (pg mL^{-1}, *n* = 3)	C18	214	206	70	217
	Fe_3O_4@SiO_2	16	18	30	25
	Fe_3O_4@SiO_2-G	0.278	0.158	0.119	0.221
LOQ (pg mL^{-1}, *n* = 3)	C18	712.62	685.98	233.1	722.61
	Fe_3O_4@SiO_2	53	60	99	83
	Fe_3O_4@SiO_2-G	0.925	0.526	0.396	0.736
EF *	C18	80	80	80	80
	Fe_3O_4@SiO_2	1000	1000	1000	1000
	Fe_3O_4@SiO_2-G	1000	1000	1000	1000

*Enrichment factor (EF) was calculated using (EF = V_{aq}/V_{org}) equation

Table 3 Repeatability and reproducibility of MSPE method for chlorinated pesticides extraction (50 mL sample include 0.1 ng mL^{-1} of each chlorinated pesticides)

Intra-day (*n*=3)	**MSPE (Fe_3O_4@SiO_2-G)**			
	Lindane	Chlorpyrifos	Hexaconazole	Azaconazole
Day 1	4.34	7.21	4.69	6.95

Day 2	8.25	5.30	6.33	3.32
Day 3	5.52	1.38	1.57	6.26
Day 4	3.58	4.13	2.16	7.08
Day 5	4.60	1.25	1.01	1.37
Inter-day (*n*=15)	8.47	9.72	4.94	8.06

Reusability of the newly synthesized adsorbent was studied for 40 times continuously in adsorption-desorption cycles. For regeneration, the adsorbent was washed sequentially with 2 mL acetone, 2 mL acetonitrile and 3 mL deionized water after each extraction process. The chlorpyrifos, hexaconazole, azaconazole and lindane were pre-concentrated at least 15 - 30 times without significant decrease in extraction efficiency.

3.7 Environmental water sample analysis

In order to assess the field application of the proposed MSPE method, chlorinated pesticides were isolated from environmental water samples i.e. tap, river, lake and sea water samples. Table 4 shows that tap water has high percent recovery as compared to the sea water due to matrix interference. Results indicated that in spite of interference the graphene-based adsorbent was still capable for absorbing 0.50 pg mL^{-1} of chlorinated pesticide from environmental water samples with good recovery 80.8-106.3% and lower RSD% (2.1-7.9%).

Table 4 Percentage recovery and precision (±RSD%) of chlorinated pesticides from different water samples for C18, $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$-G

SPE sorbent	**Samples**	**%Recovery (±RSD%, *n* = 3)***			
		Lindane	Chlorpyrifos	Hexaconazole	Azaconazole
C18	Tap water	86.6 (1.8)	86.5 (3.6)	92.4 (3.3)	90.4 (1.7)
	River water	83.5 (4.1)	83.4 (10.2)	90.3 (2.4)	88.1 (6.6)
	Lake water	87.4 (4.9)	81.1 (5.2)	83.9 (3.7)	81.3 (2.9)
	Sea water	72.5 (2.9)	73.6 (4.3)	72.0 (13.3)	71.4 (12.4)
$Fe_3O_4@SiO_2$	Tap water	95.2 (2.5)	103.7 (7.6)	102.1 (8.1)	101.2 (9.4)
	River water	92.0 (7.3)	98.6 (9.3)	99.9 (3.1)	98.0 (8.2)
	Lake water	97.4 (5.8)	101.6 (4.8)	97.2 (5.7)	97.9 (3.6)
	Sea water	88.4 (8.6)	87.9 (9.6)	83.4 (3.9)	94.7 (2.9)
$Fe_3O_4@SiO_2$-G	Tap water	104.1(2.1)	106.3 (2.1)	103.8 (3.7)	105.9 (6.5)
	River water	104.3 (5.1)	100.2 (2.5)	104.5 (4.9)	100.3 (2.9)
	Lake water	101.2 (2.0)	100.5 (7.9)	103.5 (5.3)	101.1 (4.9)
	Sea water	92.2 (3.9)	86.8 (7.1)	80.8 (3.6)	89.2 (7.7)

* The numbers in the parenthesis shows the precision (%RSD, *n* = 3).

3.8 Chromatograms of the extracted chlorinated pesticides

GC-µECD was used for the analysis of chlorinated pesticides from water samples. Fig. 11A shows the chromatogram of tap water sample. It was found that the tap water analysed do not contain the chlorinated pesticides of interest since expected peaks were not observe at expected retention times (t_R) of 5.9, 7.2, 7.9 and 8.2 min under similar GC-µECD conditions. Only a single sharp peak at 5.6 min, which belongs to internal standards (IS) propazine was observed. Fig. 11B shows the chromatogram of spiked tap water sample for extracted chlorinated pesticides using the newly synthesised $Fe_3O_4@SiO_2$-G. The data revealed that the proposed MSPE method was suitable to analyze the chlorinated pesticides in water samples since sharp peaks were observed at 5.6, 5.9, 7.2, 7.9 and 8.2 min for the propazine (IS), lindane, chlorpyrifos, hexaconazole and azaconazole, respectively.

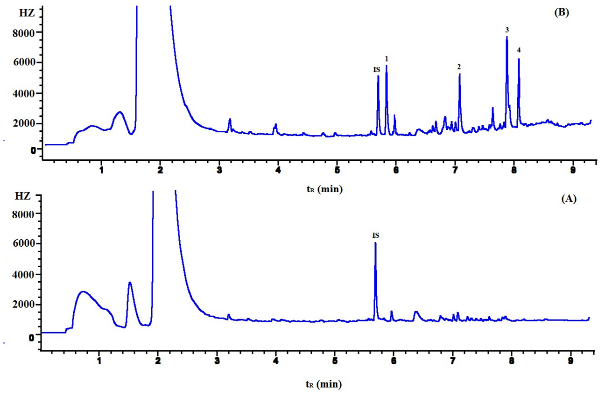

Fig. 11 GC–µECD chromatograms obtained using graphene-based MSPE from tap water samples for (A) unspiked, (B) spiked chlorinated pesticides (50 pg mL^{-1}). Peaks: 1. lindane; 2. chlorpyrifos; 3. hexaconazole; 4. azaconazole and propazine as an internal standard (IS).

3.9 Comparison with other results

For the validation of the study, the results obtained were compared with previously reported adsorbents from literatures. Comparison of LOD (Table 5) reveals that Fe_3O_4@SiO_2-G is 10-110× more sensitive compared to the previously reported adsorbents.

Table 5 Comparison of LOD of the current study with other recent MSPE sorbents

SPE sorbent	Analyte	LODs (pg mL^{-1})	Method	Detector	Ref.
Fe_3O_4@SiO_2-G	Lindane, chlorpyrifos, hexaconazole, azaconazole	0.12	MSPE	GC-µECD	This study
Pillararene-	Fusilazole,	500	MSPE	HPLC-UV	44

Fe_3O_4	cyprodinil, pyrimethanil, trifumizole				
Graphene- Fe_3O_4	Chloroacetanilide Herbicides	20.0	MSPE	GC-ECD	45
Graphene- Fe_3O_4	Herbicides	10.0	MSPE	GC-FID	46
Fe_3O_4@diocta-decyl dimethyl ammonium chloride@silica	Herbicides	70.0	MSPE	HPLC-UV	47

4. Conclusion

New graphene-based silica coated magnetic adsorbent (Fe_3O_4@SiO_2-G) was successfully synthesized and characterized using FT-IR, FESEM, EDS and XRD. The newly synthesised Fe_3O_4@SiO_2-G was successfully applied for the preconcentration of four chlorinated pesticides from aqueous media. Outstanding adsorption efficiency of 88.5%, 92.9%, 100.9% and 96.9% were achieved at pH 6.5 for lindane, chlorpyrifos hexaconazole and azaconazole, respectively. The significant adsorption capacity (13.04-18.35 mg g^{-1}) and low LOD (0.12-0.28 pg mL^{-1}) with 1000× EF confirmed that the newly synthesized Fe_3O_4@SiO_2-G is a versatile adsorbent for the preconcentration of chlorinated pesticides as compared to Fe_3O_4@SiO_2 and C18-SPE. The field studies also supported the effectiveness of this new magnetic nanocomposite adsorbent which could be useful and highly potential for the extraction of selected pesticides from real water samples.

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