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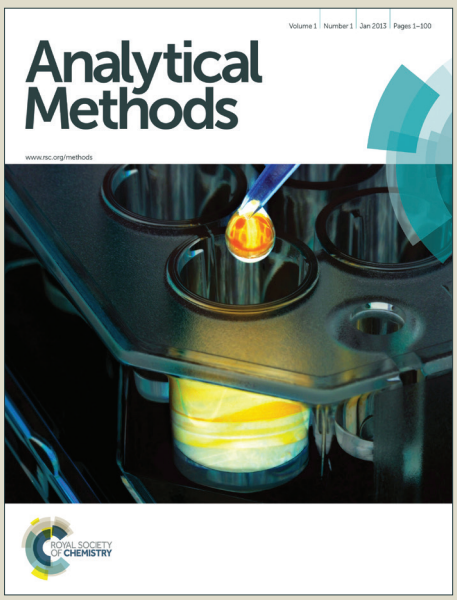

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Preparation and characterization of graphene quantum dots-Fe_3O_4 nanocomposite as an efficient adsorbent in magnetic solid phase extraction: Application to determination of Bisphenol A in water samples

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Abstract

This study describes the preparation, characterization and application of graphene quantum dots coated Fe_3O_4 (Fe_3O_4/GQDs) magnetic nanocomposite as a novel adsorbent for magnetic solid phase extraction (MSPE). The Fe_3O_4/GQDs was synthesized by a simple hydrothermal method and the resultant nanocomposite was characterized by X-ray powder diffraction, field emission scanning electron microscopy and Fourier transform infrared. The prepared nanocomposite was used for preconcentration and determination of Bisphenol A (BPA) in drinking water samples using high performance liquid chromatography with ultraviolet detection (HPLC-UV). Under the optimal extraction and analytical conditions, the developed method demonstrated a wide dynamic linear range (0.1-300 ng mL^{-1}), good linearity (R^2=0.9958), low detection limit (12.3 pg mL^{-1}) and high enrichment factor (360). The developed MSPE-HPLC-UV method was successfully applied to determination of leaked BPA from plastic bottle into the drinking water samples after exposing it to the sunlight. Satisfactory recoveries showed that the matrices under consideration do not significantly affect the extraction process. The adsorption efficiencies of Fe_3O_4/GQDs, Fe_3O_4/graphene and unmodified magnetic Fe_3O_4 nanoparticles were comparatively studied in the preconcentration and determination of BPA by HPLC-UV. Based on experimental results, Fe_3O_4/GQDs exhibit improved adsorption behaviour due to unique surface properties of GQDs.

Keywords: graphene quantum dots; Bisphenol A; magnetic nanocomposite

1. Introduction

Bisphenol A (2,2-bis(4-hydroxyphenyl)propane, BPA, is a member of diphenols in which two phenolic rings are joined together through a isopropylidene bridging group. It is the main ingredient used for the production of polycarbonate, epoxy, polyester, and polysulfone resins [1]. BPA is also used as a component of synthetic plastic materials [2] and antioxidants in glue sand inks [3, 4]. Recent studies indicate that BPA and its derivatives have high potential as endocrine disruptors in humans and wildlife [5, 6]. Thus the effect of BPA on human health through beverage, food, and water has generated great concern during the recent years.

The polarity and low concentrations of BPA in real samples cause significant problems in devising appropriate analytical methods. The literature on the analysis of BPA and its derivatives reveal that liquid-liquid extraction (LLE) [7-9] and solid-phase extraction (SPE) [10, 11] have usually been used for isolation and preconcentration of these compounds. Due to the some disadvantages such as intensive labor, time consuming, unsatisfactory enrichment factor and large quantity of toxic solvent, the use of LLE is limited in separation science. In SPE based sample preparation methods, there is a solid-phase adsorbent which adsorbs the analyte from the sample matrix and results a pre-purified, concentrated and compatible analyte with the analytical system. In some cases, due to the limited rate of diffusion and mass transfer, extraction time of SPE processes is too long.

Recently increasing number of studies have been concentrated on adsorption and separation using magnetic materials [12-14] which is so-called magnetic solid-phase extraction (MSPE). This technique is based on the combination of magnetic inorganic material and non-magnetic adsorbent material. By taking the advantage of both materials, the MSPE technology exhibits excellent adsorption efficiency and rapid separation from the matrix by an external magnetic field. On the other hand, rapid mass transfer can be obtained due to the sufficiently large contact area between the sorbents and the analytes, which is beneficial for

rapid equilibrium. Magnetic separation based on the super paramagnetic Fe_3O_4 is obviously much more convenient, economic and efficient [15-17]. The most important component of the MSPE is the adsorbent material, which dominates the selectivity and sensitivity of the method.

Graphene, a new class of 2D carbon nanomaterial with one-atom thickness, has attracted considerable attention in recent years. Due to the presence of oxygen containing groups such as hydroxyl, epoxy, carbonyl, and carboxyl groups, graphene and graphene oxide have been frequently used in separation science [18-20]. Graphene quantum dots (GQDs), are graphene sheets that are smaller than 100 nm and has been emerged as a significant research area in recent years [21-24]. GQDs having various electronic and optoelectronic properties due to quantum confinement and edge effects, making it an excellent candidate for construction of nanoscaled optical and electronic devices. GQDs are superior to common carbon materials because the nature of nano-sized single layer graphene sheets which endows them ultrahigh specific surface and makes GQDs more sensitive to the environmental changes.

In the present study, Fe_3O_4/GQDs nanocomposite was synthesized successfully and characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and field emission scanning electron microscopy (FESEM). The prepared Fe_3O_4/GQDs was employed for preconcentration of BPA from aquatic samples using MSPE method prior to determination by HPLC-UV. To evaluate the applicability of the proposed method, it was applied to the determination of released BPA from water containing bottles into the drinking water samples.

2. Experimental

2.1. Chemicals and water samples

BPA was provided by Sigma-Aldrich (St. Loius, MO, USA). Standard solutions of BPA at a concentration of 1000 mg L^{-1} was prepared in methanol and stored at 4 °C. Methanol LC-grade from Merck (Darmstadt, Germany) was used for the chromatographic analysis. $FeCl_2.4H_2O$, $FeCl_3.6H_2O$, sodium hydroxide and hydrochloric acid were used to synthesis magnetic nanoparticles (MNPs) and to adjust the solution pH. Also sodium chloride used for ionic strength studies were purchased from Merck. All other chemicals were obtained from Merck.

The recovery studies were carried out using mineral water samples that was collected from kandowan mineral water (East Azarbaijan Province, Iran). For the study of leaked BPA values from plastic bottles into the drinking water samples, the samples were stored in polyethylene bottles. Before exposing water containing bottles in front of sunlight, they were stored in refrigerator at 4 °C. The standard BPA solutions were prepared daily by diluting the stock standard solutions to the required concentrations with ultra-pure water.

2.2. Synthesis of graphene quantum dots (GQDs)

In this study, the hydrothermal method was used for the synthesis of GQDs. Firstly, graphene oxide was prepared by chemical oxidization of graphite powder according to the modified Hummers method [25, 26]. The as prepared graphene oxide was deoxidized in a tube furnace at 250 °C for 2 hours at a heating rate of 5 °C min^{-1} in a nitrogen atmosphere. The obtained graphene sheets oxidized in concentrated H_2SO_4 (10 mL) and HNO_3 (30 mL) for 15 hours under mild ultrasonication (500 W, 40 kHz). The oxidized graphene sheets were diluted and purified with microporous membrane (retained 40 micrometre) and redispersed in deionized water. Then the suspension was heated at 200 °C for 10 hours in an autoclave. The resulting black suspension was filtered with microporous membrane and a brown filtered solution was obtained. To remove larger graphene nanoparticles, the colloidal solution was dialyzed in a

dialysis bag (retained molecular weight: 3500 Da) overnight and GQDs were obtained having stability more than 3 months.

2.3. Synthesis of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared according to the modified Massart method [27] via the co-precipitation of a mixture of $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$. In particular, $FeCl_3.6H_2O$ (3.03 g) and $FeCl_2.4H_2O$ (1.13 g) were completely dissolved in 150 mL deionized water. The aqueous solution was heated to 60 $^{\circ}$C under vigorous agitation so as to obtain a clear yellow solution. Then, aqueous ammonia solution was added dropwise until the pH of the solution reached the value of 10. The reaction was maintained for an additional 30 min under vigorous stirring. N_2 was used as the protective gas throughout the experiment. After completing the reaction, the black precipitate was collected by an external magnetic field, followed by washing several times with deionized water and ethanol.

2.4. Synthesis of Fe_3O_4/GQDs nanocomposite

Firstly, GQDs (0.1 g) was dispersed in 150 mL deionized water by sonication for 10 min. Then, 1.214 g $FeCl_3.6H_2O$ was added to the GQDs solution at room temperature under a nitrogen flow with vigorous stirring. Then temperature was raised to 80 $^{\circ}$C and 0.485 g of the $FeCl_2.4H_2O$ were added slowly to the solution containing Fe_3^{+}-GQDs which was vigorously stirred for additional 30 min. Finally, the ammonia solution was added dropwise to adjust the pH of the solution at 10 for synthesis of magnetite Fe_3O_4/GQDs. Fe_3O_4/graphene was synthesized with same procedure, and just graphene was added instead of GQDs in the synthesis process.

2.5. Instrumentation

A Jasco HPLC system, consisted of a PU-1580 isocratic pump, a Rheodyne 7725i injector with a10-µL loop (Rheodyne, Cotati, CA, USA) and a UV-1575 spectrophotometric detector were used in the experiment. The chromatographic system was controlled by HSS-2000 provided by Jasco using the LC-Net II/ADC interface. The data were processed using BORWIN software (version 1.50). An analytical 250×4.6 mm ID, 5 µm particle, Perfectsil Target ODS-3 column (MZ-Analysen technik, Germany) with a ODS-3 pre-column (10×4.0 mm I.D., 5µm), which was maintained at ambient temperature, was employed for separation. X-ray diffraction (XRD) was performed by using a Brucker AXF (D8 Advance) X-ray powder diffractometer with a Cu Kα radiation source (λ=0.154056 nm) generated at 40 kV and 35 mA. Fourier transform infrared (FT-IR) spectra were recorded using a Bruker model Vector 22 FT IR Spectrometer (Ettlingen, Germany) on KBr pellets. Field emission scanning electron microscopy (FESEM) images were obtained using an S-4800 field emission scanning electron microscope (Hitachi, Tokyo, Japan).

2.6. MSPE Procedure

MSPE of all the samples involved in this study was carried out as follows: 600 mL aliquot filtered water samples at a concentration of 100 ng mL^{-1} was transferred to 1000 mL glassware beakers. Then 50 mg of Fe_3O_4/GQDs nanocomposite was added into the sample solution and was stirred for 20 min at 25 °C. Afterward an Nd-Fe-B magnet (100×50×40 mm) was positioned at the bottom of the breaker and Fe_3O_4/GQDs nanocomposite was isolated from the solution. The preconcentrated BPA adsorbed on Fe_3O_4/GQDs nanocomposite was desorbed with 1 mL methanol at 25 °C. A 10 µL of the concentrated solution was injected into the HPLC system for analysis.

2.7. Chromatographic conditions

The isocratic mobile phase consisted of methanol-water in the ratio of 70:30 v/v, flowing through the column at a constant flow rate of 1 mL min^{-1}. The eluent was monitored using UV detection at a wave length of 278 nm. The mobile phase was filtered through a 0.22 μm membrane-type GV filter (Millipore). A 40 kHz and 138W ultrasonic water bath with temperature control (sonic bath model LBS2-FALC instruments SRL Treviglio, Italy) was applied to degassing the mobile phase.

3. Results and discussion

3.1. Characterization of Fe_3O_4 and Fe_3O_4/GQDs

The surface chemistry of Fe_3O_4 and Fe_3O_4/GQDs was studied using FTIR. The typical FTIR spectra of magnetic nanoparticles were shown in Fig. 1. As can be seen the Fe-O band at Fe_3O_4/GQDs (611 cm^{-1}) shifted to higher wavelength in comparison with Fe_3O_4 (580 cm^{-1}) indicating the bonding of Fe_3O_4 to C-O-H groups on GQDs surface [28]. An absorption bond appeared at 3411 cm^{-1} corresponding to hydroxyl groups on Fe_3O_4 and Fe_3O_4/GQDs surface and the peak at 1618 cm^{-1} corresponding to vibration of water molecules adsorbed on Fe_3O_4 and Fe_3O_4/GQDs surfaces. Strong bond at 1605 cm^{-1} corresponding to stretching frequencies of C=C on Fe_3O_4/GQDs surface. Peaks at 908 cm^{-1} and 1065 cm^{-1} can be correspond to stretching frequencies of C-C at Fe_3O_4/GQDs and the peaks at 1258 cm^{-1} and 1384 cm^{-1} corresponding to the C-O stretching and O-H bending vibrations [29-31]. The presence of hydrophilic GQDs composited to the Fe_3O_4 provided an appropriate media for strong surface adsorption of BPA on the sorbent.

The crystalline structure of the synthesized MNPs was characterized by XRD. The XRD spectra of the Fe_3O_4 and theFe_3O_4/GQDs were shown in Fig. 2. The presence of the peaks corresponding to the (220), (311), (400), (422), (511), and (440) planes at the 2θ of 30, 36, 44, 54, 57 and 63 degrees confirm the formation of spinel structure [32]. Also, Fe_3O_4 and

Fe_3O_4/GQDs MNPs has similar diffraction peaks, which indicate that the crystal structure of Fe_3O_4 was not changed after modification with GQDs.

Fig. 3 shows the FESEM images of Fe_3O_4 (left) and Fe_3O_4/GQDs (right), obtained with 60000 magnifications. It can be seen that the Fe_3O_4 have nearly uniform distribution of particle size. The particle sizes of both Fe_3O_4 and Fe_3O_4/GQDs were measured in FESEM micrographs. The diameter of Fe_3O_4 is 42 nm and that of Fe_3O_4/GQDs is a little larger.

3.2. Optimization of extraction process

3.2.1. Effect of pH

The solution pH will change the surface charge of Fe_3O_4/GQDs, which is a primary factor affecting the adsorption towards the analyte. Here, the influence of the sample pH on the extraction efficiency was investigated by adjusting the pH in the range 3-12. The effect of pH value on the recoveries of BPA is shown in Fig. 4. It can be seen that the recoveries increased as the pH was increased from 3 to 5.2, and above pH 5.2, the recovery decreased. Surface charge and also the stability of the Fe_3O_4/GQDs should be considered in pH study. In more acidic media, iron oxide gets dissolved and the recoveries decreases. Also at more acidic media, due to electrostatic repulsion between Fe_3O_4 and GQDs, the stability of Fe_3O_4/GQDs decrease and the recoveries are low [33]. At high basic media, BPA exists in deprotonated form (the pK_a value of BPA in aqueous solutions is 9.8) and thus the interaction between Fe_3O_4/GQDs surface and BPA is very weak. At pH 5.2, the stability of Fe_3O_4/GQDs nanocomposite is high and tendency between the charge of GQDs functional groups and BPA is well. Therefore, pH 5.2 was selected as working pH.

3.2.2. Effect of nano-sorbent amount

The effect of Fe_3O_4/GQDs dosage on the extraction efficiency of BPA from aqueous samples is presented in Fig. 5. The peak areas increased with increasing the sorbent amount from 5 to 50 mg, and stayed unchanged with further increases. This result indicated that 50 mg of nano-sorbent was sufficient to extract BPA from aqueous solution. Therefore in the following experiments 50 mg of Fe_3O_4/GQDs was used to ensure the complete adsorption of BPA.

3.2.3. Effect of ionic strength

Generally addition of salt decreases the solubility of analytes in aqueous samples and enhances their partitioning into the adsorbent or organic phases. The effect of ionic strength on the extraction efficiency was studied by addition of sodium chloride at 0-20 % (w/v). In this study the extraction efficiency of the prepared sorbent was increased poorly with increasing sodium chloride, but precision of the process decreased with increasing the salt. Therefore, no salt was added in the followed experiments.

3.2.4. Effect of desorption solvent

After adsorption, BPA should be desorbed using an organic solvent from Fe_3O_4/GQDs for HPLC analysis. To choose an optimum desorption solvent, five solvent were evaluated (Methanol, Ethanol, Acetonitrile, Acetone and n-hexane) which are HPLC compatible solvents. The results showed that Methanol has higher extraction efficiency in comparison with other solvents (Fig. 6). Therefore, Methanol was chosen as desorption solvent.

3.2.5. Effect of desorption time

Desorption time is also a very important parameter due to its effect on desorption quantity and sensitivity. BPA adsorbed by the sorbent, were desorbed with shaking the sorbent in methanol for appropriate amount of time. The effect was studied by recording the peak area

versus desorption time. Fig. 7 shows desorption time profile from 5 to 50 min, where a 20 min desorption time appeared to be the optimum value for analysis.

3.2.6. Break through volume

Break through volume (the maximum volume that can be pre-concentrated with quantitative recovery of analyte) is a major parameter in SPE and preconcentration of samples. It significantly affects the preconcentration factor, the reproducibility and reliability of results. The break through volume was determined by a series of different volume aqueous solutions (50 to 600 mL) spiked with fixed amount of BPA at optimized conditions. Recovery of BPA was found to be quantitative when sample volume was chosen between the ranges 50-600 mL. Above 600 mL, the time required to collect the suspension with magnet increases. So, by analysing 1 mL of the final solution after the preconcentration of 600 mL sample solution, the enrichment factor (EF) was found as 360.

3.3. Validation of the method

Quantitative parameters of the proposed method such as linear range (LR), coefficient of determination (R^2), limit of detection (LOD), limit of quantification (LOQ), enrichment factor (EF) and precision were evaluated under optimum conditions (Table 1). The calibration curve were established using 600 mL deionized water spiked with different concentrations of BPA. To obtain the precision of the method, replicated analysis of spiked water samples were carried out for three times, and relative standard deviation (R.S.D.) values were calculated by the obtained peak area. The LOD, based on signal-to-noise ratio (S/N) of 3, was 12.3 pg mL^{-1} and the LOQ, based on S/N of 10, was 41 pg mL^{-1}.

3.4. Comparison

Extraction efficiency of BPA from aqueous solution with SPME method by using Fe_3O_4, Fe_3O_4/graphene and Fe_3O_4/GQDs sorbents that prepared at the same conditions are shown in fig. 8. As can be seen, Fe_3O_4 shows no efficiency in the extraction of BPA. The presence of graphene sheets in Fe_3O_4/graphene increased the extraction efficiency. The result of this observation can be related to the π-π interactions between graphene sheets and aromatic rings of BPA. When enormous graphene sheets in Fe_3O_4/graphene convert to very small GQDs sheets in Fe_3O_4/GQDs, the potential of sorbent in extraction of BPA increases outstandingly which can be related to the high surface to volume ratio, high capacity of sorbent, present of small sheets that have π-π interactions, and the present of hydroxyl functional groups that results high polarity of GQDs.

3.5. Analysis of real samples

To test the reliability of the proposed procedure, the method was employed to determine the trace amount of BPA in mineral water samples which were stored in polyethylene bottles and investigation of leakage of BPA from polyethylene bottles to mineral water after remaining in front of sunlight. The first analysis demonstrated 0.21 ng mL^{-1} BPA in fresh mineral water sample (Fig. 9A). After one week that waters were kept in front of sunlight, the amount of BPA in water samples were increased to 3.4 ng mL^{-1} that shows the leakage of BPA from polyethylene bottles to water samples (Fig. 9B). Fig. 9C shows the chromatogram of water sample in polyethylene bottle after exposing to sunlight for one week and spiked with 20 ng mL^{-1} BPA.

The accuracy of the method was evaluated by the recovery test which was carried out with spiked mineral water samples. The recoveries for the analysis of BPA in spiked water samples using the proposed method was shown in Table 2. According to these studies the

recoveries for BPA were in the range 96.3% to 104.9% with R.S.D. values between 3.6% and 5.2%.

4. Conclusions

In this study Fe_3O_4/GQDs magnetic nano-sorbent was synthesized as a novel adsorbent for magnetic solid phase extraction and applied for efficient enrichment of trace BPA from water samples. The efficiency of Fe_3O_4/GQDs in BPA preconcentration was compared with Fe_3O_4/graphene which resulted the improved adsorption behaviour of GQDs in comparison with graphene. The results showed that the proposed method is suitable for rapid preconcentration and determination of BPA from large volume samples. The method was successfully applied to determination of leaked BPA from plastic bottle into the drinking water samples. The high breakthrough volume of water samples and the small volume of the elution permitted to get high enrichment factor. Due to the high capacity and surface to volume ratio of GQDs in comparison with another carbon based materials, it can be used as an efficient sorbent in separation science.

Acknowledgement

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Figure captions

Fig. 1. FTIR spectra of the Fe_3O_4 and Fe_3O_4/GQDs MNPs.

Fig. 2. XRD patterns of Fe_3O_4 and Fe_3O_4/GQDs MNPs.

Fig. 3. FESEM images of Fe_3O_4 and Fe_3O_4/GQDs MNPs.

Fig. 4. The effect of pH on the extraction efficiency.

Fig. 5. The effect of Fe_3O_4/GQDs dosage on extraction efficiency of BPA.

Fig. 6. The effect of desorption solvent on extraction efficiency.

Fig. 7. The effect of desorption time on extraction efficiency.

Fig. 8. Comparison of extraction efficiency of BPA with Fe_3O_4, Fe_3O_4/graphene and Fe_3O_4/GQDs sorbents.

Fig. 9. The chromatograms of (A) fresh mineral water; (B) mineral water contained in plastic bottle and exposed directly to sunlight for one week; (C) mineral water contained in plastic bottle and exposed directly to sunlight for one week and spiked with 20 ng mL^{-1} BPA.

Table. 1. Precision, LOQ, LOD, EF, linearity, and regression equation obtained in the analysis of BPA.

Table 2. Results of determination and recoveries of mineral water samples spiked with BPA.

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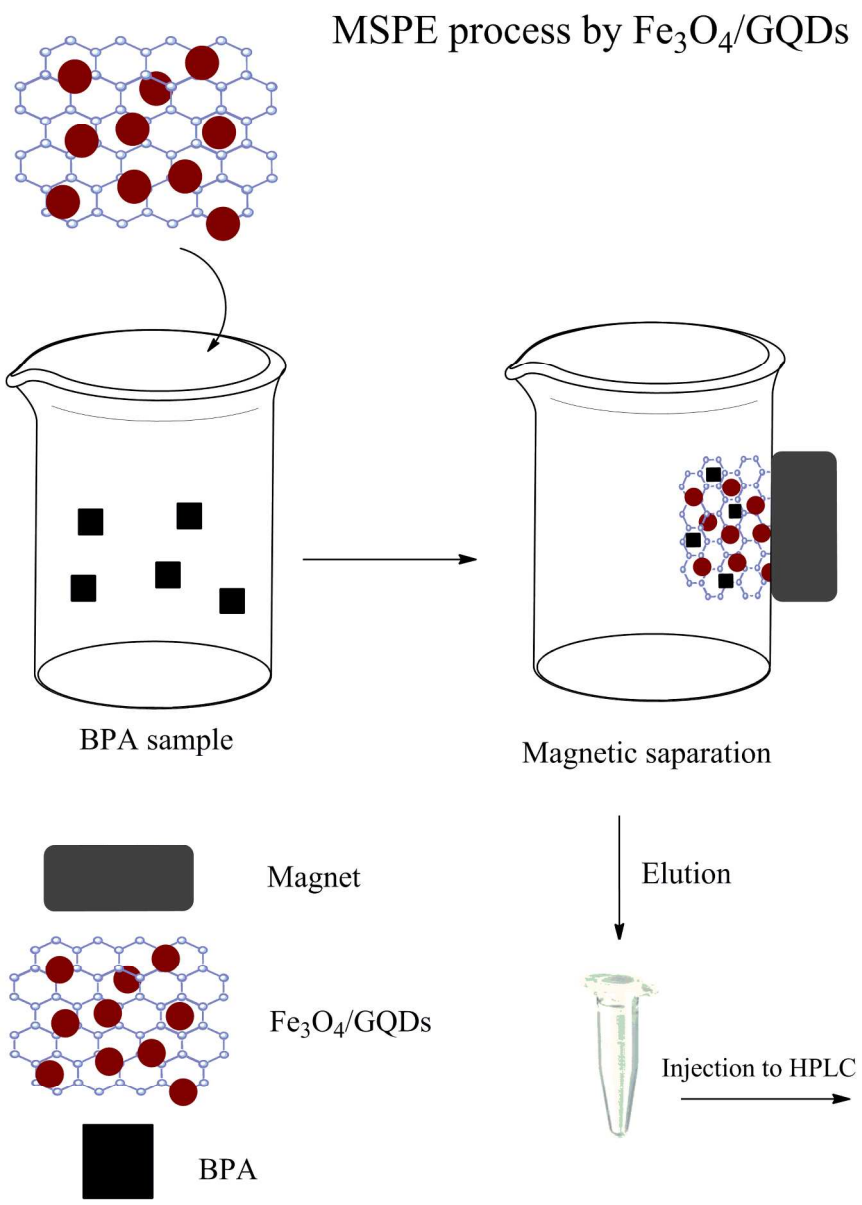

MSPE process by Fe3O4/GQDs
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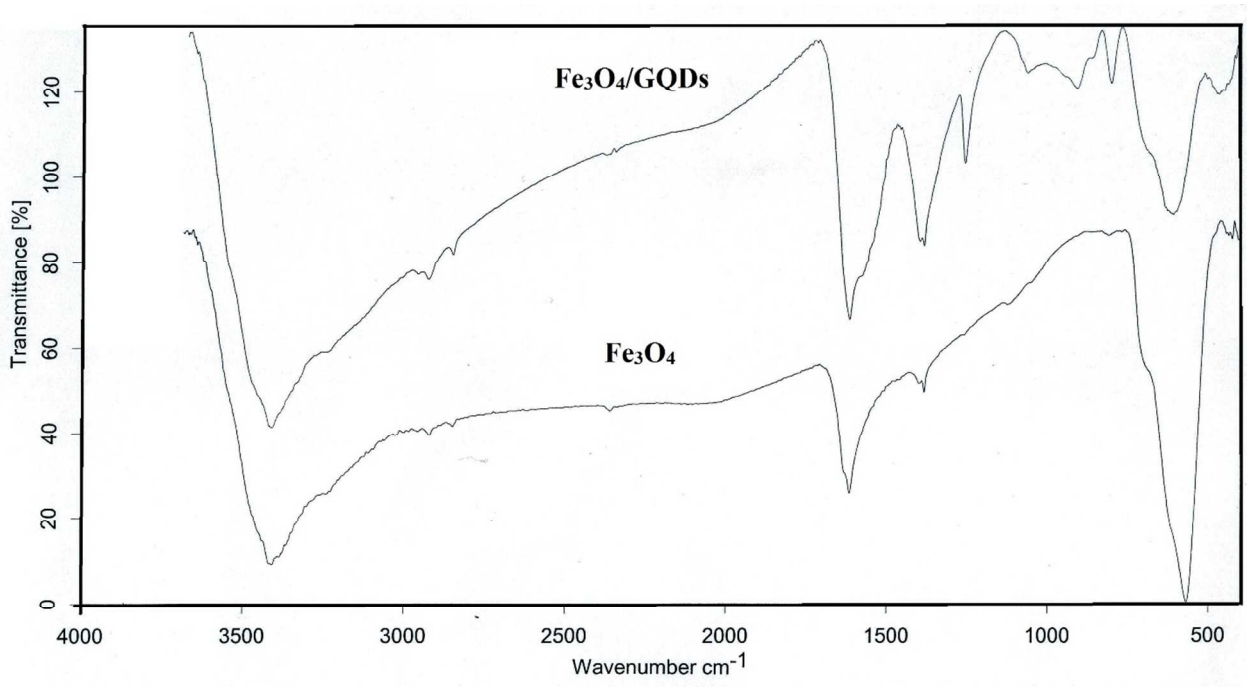

Fig. 1

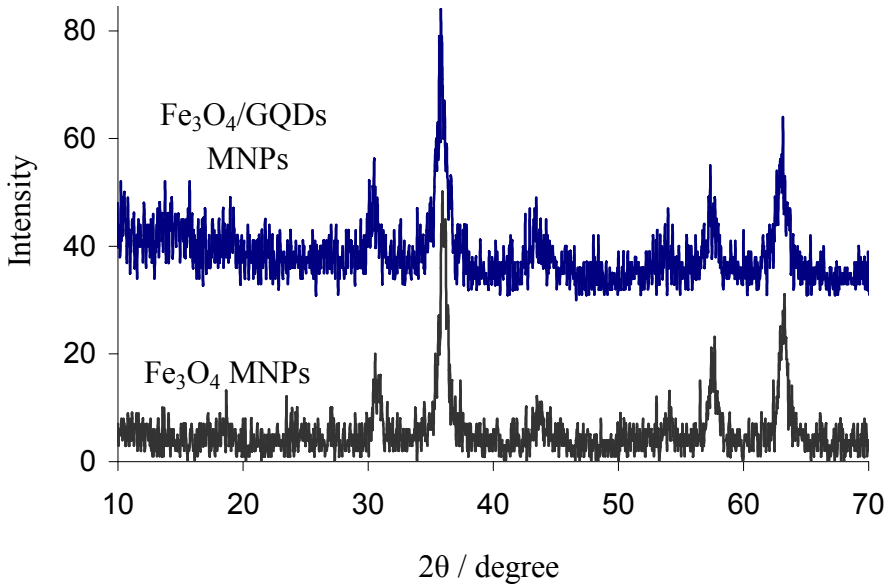

Fig. 2

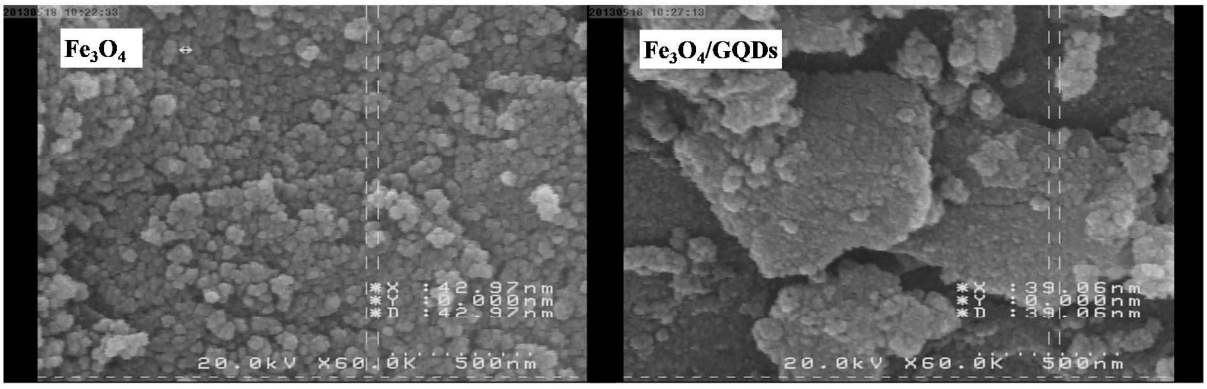

Fig. 3

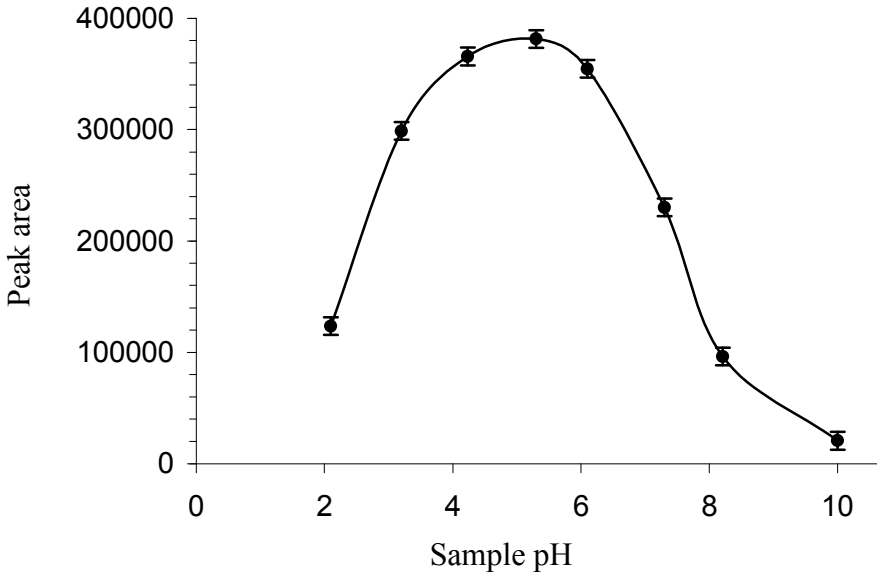

Fig. 4

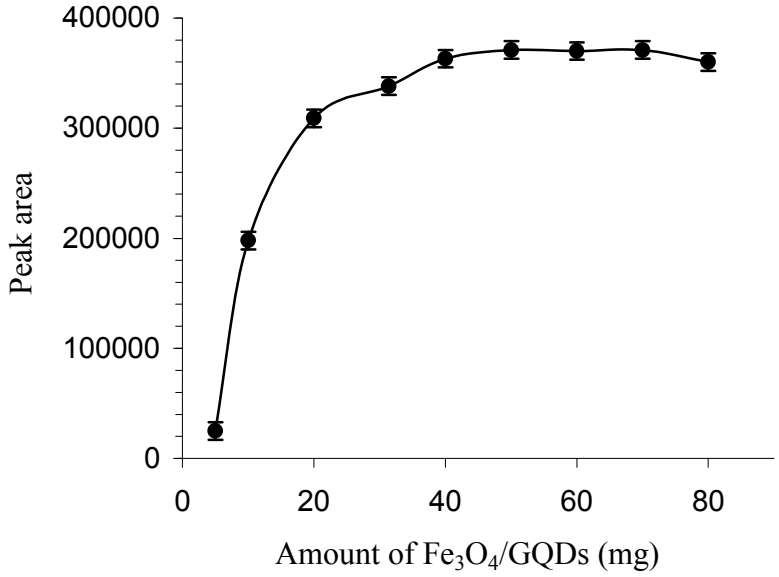

Fig. 5

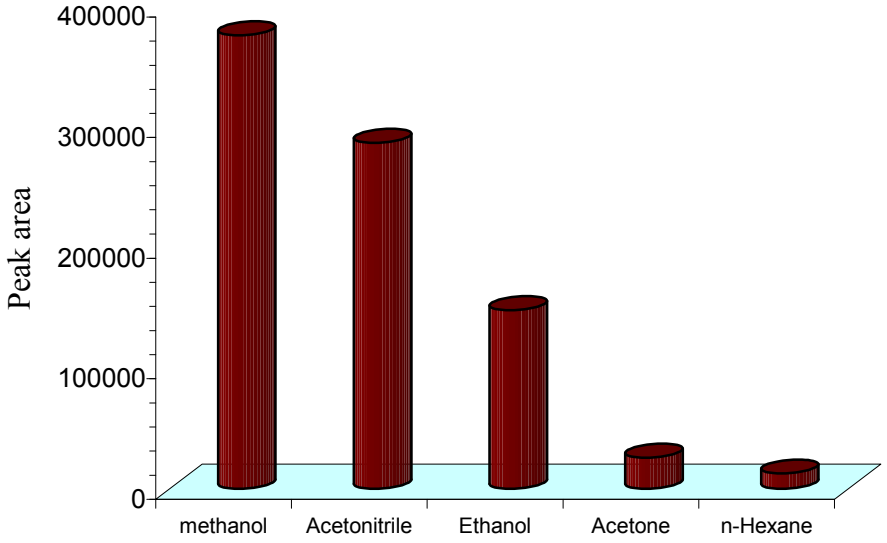

Fig. 6

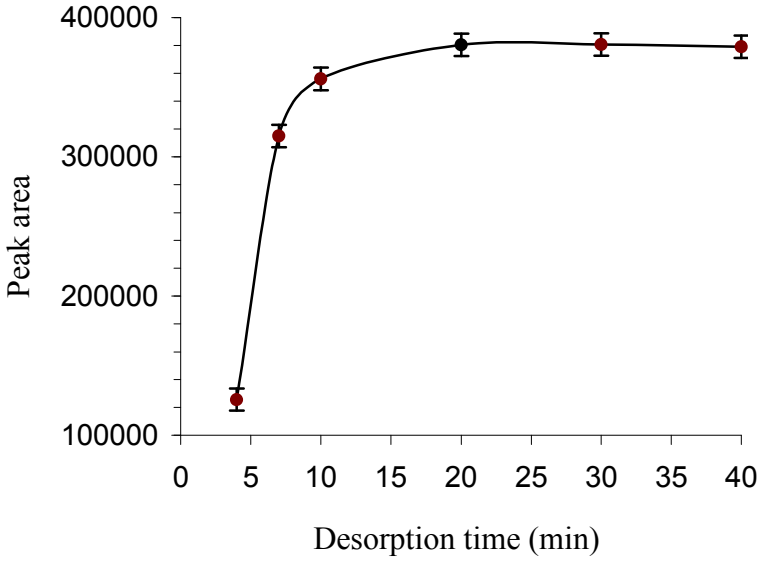

Fig. 7

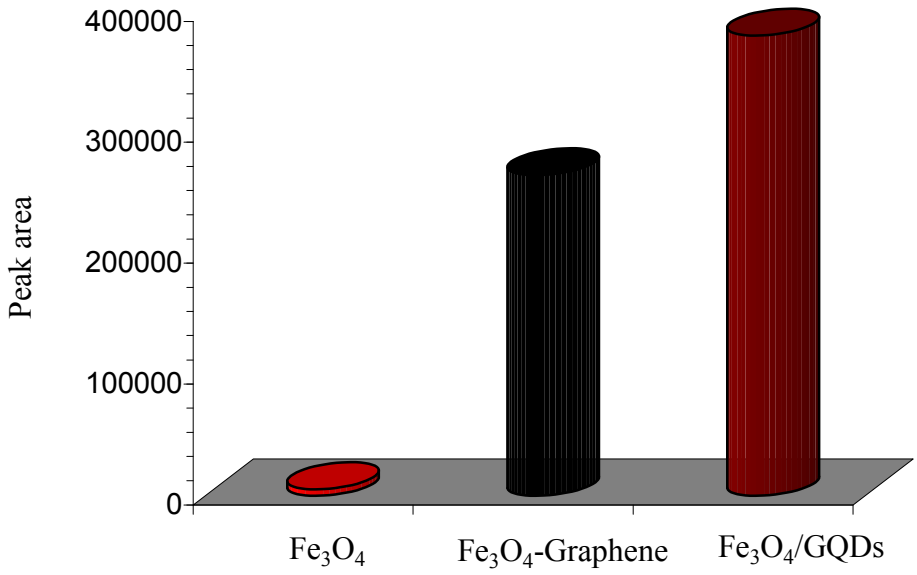

Fig. 8

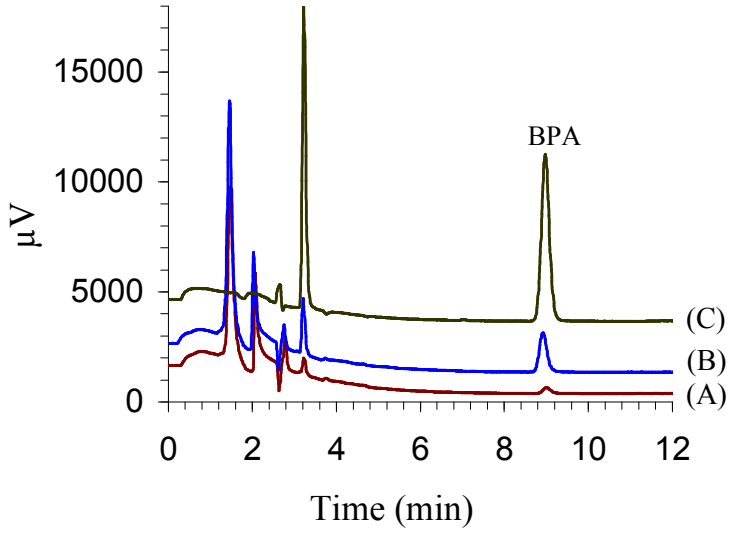

Fig. 9

Table. 1. Precision, LOQ, LOD, EF, Linearity, and regression equation obtained for BPA analysis

Analyte	*RSD (%)*	*LOQ (pg mL^{-1})*	*LOD (pg mL^{-1})*	*EF*	*LR (ng mL^{-1})*	*Regression equation*
BPA	4.3	41	12.3	360	0.1-300	Y= 3606 X +20266

Table 2. Results of determination and recoveries of mineral water samples spiked with BPA

Amounts of BPA (ng mL^{-1})	*R.S.D. (%)*	*Recovery (%)*
5	5 .2	96.3
10	4.3	104.9
20	3.6	98.5