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Q9 **A nanocomposite consisting of silica-coated magnetite and**  
 2 **phenyl-functionalized graphene oxide for extraction of**  
 3 **polycyclic aromatic hydrocarbon from aqueous matrices**

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**ABSTRACT**

In this study, graphene oxide was covalently immobilized on silica-coated magnetite and then 15  
 modified with phenylethylamine to give a nanocomposite of type  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{GO}-\text{PEA}$  that 16  
 can be applied to the magnetic solid-phase extraction of polycyclic aromatic hydrocarbons 17  
 (PAHs) from water samples. The resulting microspheres ( $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{GO}-\text{PEA}$ ) were 18  
 characterized by Fourier transform-infrared spectroscopy, scanning electron microscopy 19  
 (SEM), CHNS elemental analysis, and vibrating sample magnetometry (VSM) techniques. The 20  
 adsorbent possesses the magnetic properties of  $\text{Fe}_3\text{O}_4$  nanoparticles that allow them easily to 21  
 be separated by an external magnetic field. They also have the high specific surface area of 22  
 graphene oxide which improves adsorption capacity. Desorption conditions, extraction time, 23  
 amount of adsorbent, salt concentration, and pH were investigated and optimized. Following 24  
 desorption, the PAHs were quantified by gas chromatography with flame ionization detection 25  
 (GC-FID). The limits of detection (at an  $S/N$  ratio of 3) were achieved from 0.005 to 0.1  $\mu\text{g/L}$  with 26  
 regression coefficients ( $R^2$ ) higher than 0.9954. The relative standard deviations (RSDs) were 27  
 below 5.8% (intraday) and 6.2% (inter-day), respectively. The method was successfully applied to 28  
 the analysis of PAHs in environmental water samples where it showed recoveries in the range 29  
 between 71.7% and 106.7% (with RSDs of 1.6% to 8.4%, for  $n = 3$ ). The results indicated that the 30  
 $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{GO}-\text{PEA}$  microspheres had a great promise to extraction of PAHs from different 31  
 water samples. 32

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48 **Introduction**

49 Polycyclic aromatic hydrocarbons (PAHs) are an important  
 50 class of organic compounds which contain two or more fused  
 51 aromatic rings. These compounds are environmental persistent  
 52 pollutants with high toxicity, mutagenicity and carcinogenicity  
 53 that arising from different sources such as combustion of fossil  
 54 fuel and biomass, oil spills and some industrial processes  
 55 (Zakaria et al., 2002; Zhao et al., 2009). Since PAHs are non-polar

and very hydrophobic compounds with low water solubility, 56  
 they commonly exist at low concentrations in aquatic systems 57  
 (De Maagd et al., 1998). Therefore, sample pretreatment is often 58  
 required for preconcentration of PAHs from water samples 59  
 prior to instrumental analysis. Up to now, various sample 60  
 preparation techniques have been developed for extraction 61  
 and enrichment of PAHs (Brum et al., 2008; Charalabaki et al., 62  
 2005; Doong et al., 2000; Lundstedt et al., 2000; Oleszczuk and 63  
 Baran, 2004; Popp et al., 2001; Shi and Lee, 2010; Tavakoli et al., 64

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2008). Among them, solid-phase extraction (SPE) is an increasingly useful technique for extraction and preconcentration of PAHs, due to its advantages including simplicity, good extraction efficiency and low consumption of organic solvents (Kefi et al., 2011; Ma et al., 2010; Marcé and Borrull, 2000; Wang et al., 2007, 2014). But the traditional SPE is labor and time-consuming due to its limited diffusion and mass transfer rate. Recently, a new mode of SPE named magnetic solid-phase extraction (MSPE) has been developed to overcome these limitations (Chen et al., 2013; Huo and Yan, 2012). In the MSPE procedure, the magnetic adsorbent is dispersed in a sample solution containing the target analytes instead of loading into a cartridge. This avoids limited mass transfer and/or blocking cartridges that usually occurs in traditional SPE (Jiao et al., 2012; Li and Qi, 2014; Román et al., 2011). Furthermore, magnetic particles can be easily separated by using an external magnet without additional centrifugation or filtration of the sample solution. This makes the sample treatment procedure easier and faster.

As a novel carbon nanomaterial, graphene (G) has gained remarkable attentions in analytical science in recent years because of its unique properties in term of chemical and mechanical stability, large surface area and  $\pi$ -electron rich structure (Liu et al., 2012b). Graphene oxide (GO), as a precursor for G, can interact with many compounds through electrostatic interaction, hydrogen bonding, and  $\pi$ - $\pi$  stacking forces (Sitko et al., 2013). However, unlike graphene, GO contains many oxygen-functional groups, such as epoxy and hydroxyl groups, enabling good dispersion of GO in many solvents (Chen et al., 2012). Also, the carboxyl and carbonyl groups on the edges of surfaces, simplify reaction with other functional groups (Wang et al., 2011). Thus, GO is an ideal candidate for use as adsorbent in SPE.

The combination of easy separation of magnetic NPs ( $\text{Fe}_3\text{O}_4$ ) and high adsorption capacity of GO can led to produce the adsorbents with excellent separation properties. Several research groups have synthesized magnetic GO (or G) with different methods for extraction of various compounds (Han et al., 2012; Junyong et al., 2013; Liu et al., 2011; Wang et al., 2012; Yan et al., 2014). However, in many methods,  $\text{Fe}_3\text{O}_4$  particles were decorated on the surface of GO (or G) which causes some problems. The unprotected particles can easily be oxidized under harsh extraction conditions and lose their magnetism at long-term use. These problems can be avoided with coating the magnetic core with suitable materials. Among many developed protective shell materials, silica has been considered as the most ideal substance because of its availability, cheapness, good chemical stability, biocompatibility and flexibility in surface modification (Ma et al., 2012; Zhang et al., 2011). Recently, some research groups (Liu et al., 2012a; Luo et al., 2011) have prepared  $\text{Fe}_3\text{O}_4@SiO_2/G$  by physical adsorption of G onto silica-coated magnetic particles and applied them for extraction of various compounds. However, these synthesized nanomaterials are not stable enough for repeated uses due to physical bonding of G. On the other hand, hydrophobic properties of G limit its dispersability in aqueous solutions while in a SPE mode the compatibility of adsorbent with sample solutions is a very important factor. Therefore, designing suitable adsorbents with good affinity toward the target analytes as well as compatibility with sample matrix is an essential issue.

In this work, a superparamagnetic nanomaterial,  $\text{Fe}_3\text{O}_4@SiO_2@GO-PEA$ , was synthesized via covalent bonding of the GO nanosheets with silica-coated  $\text{Fe}_3\text{O}_4$  microparticles, and after that the GO surfaces were chemically modified with phenylethylamine (PEA). The existence of oxygen-functional groups on the surfaces of GO is responsible for hydrophilicity and make it more suitable for extraction and separation procedures. But the oxygen-functional groups interrupt the  $sp^2$ -hybridized structure of GO, resulting in weaker  $\pi$  interactions with organic molecules. Therefore, the modification of GO with PEA promotes  $\pi$  interactions of the adsorbent with analytes. So, the synthesized  $\text{Fe}_3\text{O}_4@SiO_2@GO-PEA$  has advantages of high surface area, good water dispersability of GO, and magnetic property of  $\text{Fe}_3\text{O}_4$  nanoparticles. Moreover, the magnetic microspheres are sufficiently stable for repeated uses because of covalent bonding of GO with  $\text{Fe}_3\text{O}_4@SiO_2$ . The performance of the  $\text{Fe}_3\text{O}_4@SiO_2-GO-PEA$  as an adsorbent was evaluated for extraction of ten PAHs in MSPE procedure from complex water matrices.

## 1. Experimental

### 1.1. Reagents and materials

All chemicals including tetraethyl orthosilicate (TEOS), amino propyltriethoxysilane (APTES), N(3-dimethylaminopropyl)-N-ethyl-carbodiimide hydrochloride (EDC), N-hydroxysuccinimide (NHS), ethylene glycol, 2-phenylethylamine (PEA), acetonitrile (ACN), acetone (AC), tetrachloroethylene ( $\text{C}_2\text{Cl}_4$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), n-hexane, toluene, ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), and sodium acetate (NaAc) were prepared from Merck Chemicals (Darmstadt, Germany). A certified mixture of PAHs (EPA 525 PAH Mix A) containing of 500  $\mu\text{g}/\text{mL}$  of each PAH in methylene chloride was purchased from Sigma Aldrich (St. Louis, MO, USA). The working standard solution (50 mg/L) was prepared in methanol and stored at 4°C before use. Working solutions were prepared daily by appropriate dilution of the stock solutions.

#### 1.1.1. Real samples

A river water sample was collected from the Zayanderud River (Isfahan, Iran); a wastewater sample was taken from municipal wastewater channel (Tehran, capital of Iran); and the hookah water sample was taken from a hookah water pipe that had been used for 30 min. The collected samples were filtered through a 0.45- $\mu\text{m}$  membrane and stored in dark glass bottle at 4°C until used for analysis.

### 1.2. Instrumentation

The GC analyses of the PAHs were carried out using a gas chromatograph (7890, Agilent technologies, Santa Clara CA, USA) equipped with a flame ionization detector (FID) and a split/splitless injector. The chromatographic separations of the extracted PAHs were performed on a HP-5 capillary fused silica column (length, 30 m; internal diameter, 0.32 mm; film thickness, 0.25  $\mu\text{m}$ ; stationary phase, 5% phenyl-95% methyl polysiloxane) with helium (99.999%) as carrier gas at a flow-rate of 1 mL/min. The column temperature was programmed as follows: 90°C for 5 min then raised to 270°C at 20°C/min and

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