Magnetized graphene layers synthesized on the carbon nanofibers as novel adsorbent for the extraction of polycyclic aromatic hydrocarbons from environmental water samples

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ARTICLE INFO

ABSTRACT

The application of magnetized graphene (G) layers synthesized on the carbon nanofibers (CNFs) (m-G/CNF) was investigated as novel adsorbent for the magnetic solid-phase extraction (MSPE) of polycyclic aromatic hydrocarbons (PAHs) in water samples followed by gas chromatography–flame ionization detector (GC–FID). Six important parameters, affecting the extraction efficiency of PAHs, including: amount of adsorbent, adsorption and desorption times, type and volume of the eluent solvent and salt content of the sample were evaluated. The optimum extraction conditions were obtained as: 5 min for extraction time, 20 mg for sorbent amount, dichloromethane as desorption solvent, 1 mL for desorption solvent volume, 5 min for desorption time and 15% (w/v) for NaCl concentration. Good performance data were obtained at the optimized conditions. The calibration curves were linear over the concentration ranges from 0.012 to 100 ng mL^{-1} with correlation coefficients (r) between 0.9950 and 0.9967 for all the analytes. The limits of detection (LODs, S/N = 3) of the proposed method for the studied PAHs were 0.004–0.03 ng mL^{-1}. The relative standard deviations (RSDs) for five replicates at two concentration levels (0.1 and 50 ng mL^{-1}) of PAHs were ranged from 3.4 to 5.7%. Appropriate relative recovery values, in the range of 95.5–99.9%, were also obtained for the real water sample analysis.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a large group of organic compounds that are included in the European Union (EU) and the US Environmental Protection Agency (US EPA) priority pollutant list because of their mutagenic and carcinogenic properties [1]. They are formed mainly as a result of pyrolytic processes, especially the incomplete combustion of organic materials such as coal, gas, garbage, meats, oil, tobacco, and wood [2]. The PAH levels in environmental water samples are usually very low because of their very low water solubility and high hydrophobicity. Thus it is necessary to extract them from samples before instrumental analysis.

Sample pretreatment prior to the analysis is considered as the most critical step in the overall analytical process since it plays a key role in analyte extraction, pre-concentration, and cleanup from co-existing species. Liquid–liquid extraction (LLE) [3,4] and solid phase extraction (SPE) [5,6] have been the most widely used procedures for these purposes in the determination of PAHs in water samples. Classic preconcentration methods have been replaced in the last years by new sample preparation microextraction techniques, which are simpler, cleaner and quicker, and which consume low quantities of solvent. In this sense, many new methods have been developed and applied to PAHs extraction in different sample matrices, such as solid-phase microextraction [7–9], liquid-phase microextraction [10,11], stir bar sorptive extraction [12–15], micro-solid-phase extraction [16], and more recently magnetic solid-phase extraction (MSPE) [17,18].

Recently, MSPE has attracted increasing interest worldwide. Owing to the nanoscale particle size, the magnetic nanoparticles (MNPs) commonly possess large surface area and short diffusion pathway, which may result in large extraction capacity and high extraction efficiency. Additionally, the MNPs can be quickly isolated from matrix solution via an external magnetic field after extraction. Among the MNPs, Fe_3O_4 is the most of used supports due to their good biocompatibility, low toxicity, high surface area, rapid magnetic susceptibility and ease of preparation [19,20].

In recent years, carbon nanomaterials have received considerable attention primarily because of their unique properties. Carbon

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nanomaterials have been investigated as novel and interesting sorption materials since their discovery [21–23]. In recent years, great efforts have been focused on applying the methods of covalent or non-covalent functionalization to improve the solubility and selectivity of the carbon nanomaterials in solvents or polymers [24].

Magnetic carbon-based nanomaterials, combination of magnetic nanoparticles with carbon-based materials, have many unique properties including good thermal stability, tunable miscibility, and good extraction capability, which make them as promising materials for identifying and addressing many environmental challenges such as wastewater treatment, heavy metal removal, and pollutant adsorption [25–28]. The carbon-based nanomaterials are superior for constructing highly efficient adsorbents for adsorbing pollutants due to their large specific surface areas, porous and layered nanostructure, and ease of functionalization, while magnetic materials have intrinsic advantages for the separation of pollutants from adsorbents because magnetic separation process is a simple, efficient, and economic process.

In this work, for the first time, we reported the preparation, characterization and application of magnetized graphene (G) layers synthesized on the branched carbon nanofibers (CNFs) (m-G/CNF) as novel adsorbent for the extraction of PAHs from water samples. The main aim of this study was to develop a MSPE adsorbents preparation method and investigate the extraction performance of the synthesized adsorbents to target analytes.

2. Experimental

2.1. Chemicals and reagents

The methanol, toluene, *n*-hexane, dichloromethane, chloroform, ferric chloride ($FeCl_3 \cdot 6H_2O$), ferrous chloride ($FeCl_2 \cdot 4H_2O$), Nitric acid (60%), ammonia and sodium chloride (NaCl) were purchased from Merck (Darmstadt, Germany). Also, PAHs include naphthalene, 2-methylnaphthalene, fluorene, phenanthrene, and 2-bromonaphthalene were purchased from Merck (Darmstadt, Germany). A high purity acetylene (C_2H_2) as a carbon gas source (99.999%, Smart biogas company, Malaysia), nitrogen (air product, 99.9995) as a carrier gas, and copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$) and nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) as catalyst sources were utilized in the experimental part. Stock solutions ($100\,mg\,L^{-1}$) of PAHs were prepared in methanol and stored in the dark at 4 °C. Working solutions were prepared by the dilution of the stocks in the deionized water.

2.2. Instrumentation

A Shimadzu gas chromatograph (Shimadzu-17A, Tokyo, Japan) equipped with a split/splitless inlet and flame ionization detector (FID) was used for the determination of PAHs. The temperatures of the injector and detector were set at 300 °C. The carrier gas was N_2 (99.999%) with constant flow of $1\,mL\,min^{-1}$. Chromatographic separation was accomplished with a Shimadzu Hicap CBP-5-M25–025 (5% biphenyl + 95% ploydimethylsiloxane) fused-silica column (25 m, length; 0.25 mm I.D.; 0.22 μm, film thickness). The GC oven was programmed as follow: 100 °C (2 min held), ramp to 220 °C at 40 °C min^{-1} and then held for 1 min. A magnetic stirrer, model MR HCl-standard (Heidolph, Germany), with speed 0–1400 rpm, was employed for stirring samples during the extraction. For dispersion of nanoparticles in the sample solution, an ultrasonic bath (Parsonic 15S, Pars Nahand Engineering Co.), was used at a frequency of 28 kHz. For sorbent collection and magnetic decantation, an Nd-Fe-B magnet (2 × 2 × 1 cm, 1.4 T) was used. Scanning electron microscopy (SEM) (Hitachi S-3400 N, Japan) and transmission electron microscopy (Leo, model 912 AB, Germany)

were used to characterize the morphology and size of the prepared nanomaterials. The specific surface areas of the nanomaterials were measured using nitrogen Brunauer–Emmett–Teller (BET) adsorption instrument (BELSORP-mini II analyzer).

2.3. Synthesis of m-G/CNF nanocomposites

2.3.1. Synthesis of graphene layers on the branched carbon nanofibers grown on carbon fiber (G/CNF)

The chemical vapor deposition (CVD) method was applied for the synthesis of the CNF and graphene on the carbon fibers (CFs) at atmospheric pressure. In this study, commercially available, polyacrylonitrile (PAN)-based carbon fibers (Toho Tenax America, Inc.) with length about 0.5 mm and 6.5 micrometer in diameter were utilized as a substrate. First, the CFs were immersed into a mixture of copper nitrate trihydrate and nickel nitrate hexahydrate solution in acetone (70%, 30%) and followed by ultrasonic agitation for 2 h. In order to activation of catalyst, the CFs were heated at 200 °C under air flow for 2 h. Then CFs were coated with CNF via CVD through the thermal decomposition of acetylene (C_2H_2) as the carbon precursor gas. The CNF growth process is performed by flowing 100 sccm H_2, 100 sccm N_2, and 50 sccm C_2H_4 over the Ni-Cu-coated CF substrates at 600 °C inside a reactor for 30 min. The C_2H_2 at high temperature decomposed to C atoms and H_2 molecules on the surface of the catalyst. The C atoms on the surface of catalyst are attached together and so sp^2 network is formed. After that the flow of acetylene was stopped and temperature was increased to 1050 °C. When the temperature reach to 1050 °C, again the acetylene was inserted and the graphene layers were synthesized on the produced CNF surface. Fig. 1 shows the schematic diagram of preparation procedure of G/CNF.

2.3.2. Oxidization of G/CNF

1 g of pristine G/CNF was added to a concentrated nitric acid (60%, 50 mL). Then, the mixture was refluxed for 24 h to introduce carboxyl groups onto carbon nanomaterials surface. Afterwards, the oxidized G/CNF solution was rinsed with distilled water for five times until the pH value reached neutral. The resulting G/CNF were separated from the solution by filtration and dried in vacuum at 60 °C for further use.

2.3.3. Preparation of m-G/CNF nanocomposites

The Fe_3O_4-G/CNF nanocomposites were prepared by the simple co-precipitation method. In this case, 2.1 g of $FeCl_2 \cdot 4H_2O$ and 5.8 g of $FeCl_3 \cdot 6H_2O$ were dissolved in 100 mL of deionized water. The mixture was heated at 80 °C for 10 min and then, 0.5 g of oxidized G/CNF was added to the solution under nitrogen atmosphere. After that, 20 mL of ammonia solution (25% w/w) were added and the mixture was stirred for 60 min. The precipitate was isolated from the solution by applying an external magnet, washed with deionized water (three times) and finally dried in a vacuum oven at 60 °C for 12 h.

2.4. Magnetic SPE procedure

Twenty milliliters of water sample spiked with PAHs was added into a 25 mL vial, and then an amount of 20 mg of m-G/CNF nanocomposites was added. The mixture was sonicated for 10 s to accelerate their dispersion in the solution. The mixture was stirred vigorously for 5 min, and in this process, target analytes were adsorbed onto m-G/CNF, through π–π interactions. The magnet placed on the outer wall of the vial in order to collect the nanoparticles and then the supernatant was decanted. Subsequently m-G/CNF sorbents washed with ultrapure water and dried under a nitrogen stream. Next, the PAHs were eluted from the m-G/CNF with a 1 mL of dichloromethane under stirring during 5 min.