



Analysis of phthalate acid esters in environmental water by magnetic graphene solid phase extraction coupled with gas chromatography–mass spectrometry



Qing Ye*, Linhai Liu, Zhongbao Chen, liming Hong

Department of Chemistry, Shangrao Normal University, Shangrao 334001, China

ARTICLE INFO

Article history:

Received 19 August 2013

Received in revised form

29 December 2013

Accepted 31 December 2013

Available online 6 January 2014

Keywords:

Magnetic graphene

Phthalate acid esters

Magnetic solid phase extraction

Environmental water

ABSTRACT

In this work, magnetic graphene composites were synthesized via a simple hydrothermal reaction. The as-prepared composites were successfully applied as an effective adsorbent for the preconcentration of seven phthalate acid esters (PAEs) in environmental water samples prior to gas chromatography–mass spectrometry (GC–MS) analysis. The magnetic graphene composites had a unique structure in which magnetite particles were deposited on graphene sheets. This unique structure not only provided strong magnetic responsiveness for the separation but also prevented the self-aggregation of graphene. The magnetic graphene composites had several advantages, such as large surface area, fast separation ability, and high peak intensity for aromatic analytes; these properties are attributed to the distinct structure of magnetic graphene composites, which comprises p-conjugated networks with a highly exposed surface. Various parameters, including eluting solvent and volume, absorbent amount, extraction time and elution time, were optimized. Validation experiments showed that the optimized method presented good linearity ($r > 0.997$), satisfactory precision (RSD < 8.5%), and high recovery (88–110%). The limits of detection were from 0.010 $\mu\text{g/L}$ to 0.056 $\mu\text{g/L}$, and the limits of quantification were from 0.035 $\mu\text{g/L}$ to 0.19 $\mu\text{g/L}$. The proposed method had these advantages of simplicity, good sensitivity, and high efficiency. Finally, the proposed was successfully applied to the analysis of PAEs in real water samples.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Phthalate acid esters (PAEs) are widely used as polymer additives (plasticizers) in the manufacture of plastics, medical devices, building materials, children's toys, and cosmetics to improve their flexibility [1]. PAEs are not chemically bound to plastic. They can readily leach, migrate, or evaporate into various environmental matrices. Their accumulation in natural waters causes wide distribution within aqueous systems, such as rivers, lakes, and ground waters. PAEs also influence the ecological environment [2,3]. These compounds, which can be readily absorbed through the skin, are hazardous to human health affect fertility. PAEs reportedly cause adverse effects on human health. Several studies have shown that PAEs can produce effects similar to those of estrogen, causing feminization of male infants and disturbances in genital development and testes maturation [4–6]. In animals, these esters have shown teratogenic, carcinogenic, reproductive and developmental effects. However, the effects of PAEs in humans remain controversial [7–9]. Determination of PAEs in environmental water has become an

urgent task because of the toxic or carcinogenic characteristics of these compounds. Gas chromatography (GC) and liquid chromatography (HPLC) coupled with mass spectrometry (MS) are the most widely used techniques for the trace analysis of PAEs. As we know, extraction and enrichment of PAEs in samples were needed prior to GC–MS or HPLC–MS analysis.

Liquid–liquid extraction (LLE) and solid-phase extraction (SPE) are two classical and widely used sample preparation methods for the analysis of PAEs [10–14]. However, LLE has several disadvantages: it is time-consuming, promotes loss of target analytes, and requires consumption of large amounts of hazardous organic solvents. SPE often suffers from plugging of the cartridge and consumption of large of toxic solvents at the elution step [15,16]. Therefore, many SPE or LLE-based microextraction techniques requiring little or no solvent have been developed for the analysis of PAEs over the past decades. These methods include solid-phase microextraction [17–21], electro-enhanced solid-phase microextraction [22], liquid-phase microextraction [23,24], air-assisted liquid–liquid microextraction [25], low-density solvent-based vortex-assisted surfactant-enhanced-emulsification liquid–liquid microextraction [26], vortex-assisted micro-solid-phase extraction followed by low-density solvent based dispersive liquid–liquid microextraction [27], and dispersive liquid–liquid microextraction [1,4].

* Corresponding author. Tel.: +86 793 8337897; fax: +86 7938150694.
E-mail address: sryq6333@163.com (Q. Ye).

A new mode of SPE called magnetic solid-phase extraction (MSPE) was recently developed. This method has several advantages over traditional SPE. In MSPE, separation process can be performed directly in crude samples containing suspended solid materials without the need for additional centrifugation or filtration, which makes the separation easier and faster. Therefore, MSPE may be widely applied in many fields [28–35].

Graphene is a new allotropic member of carbon, discovered in 2004; it has attracted tremendous attention from both the experimental and theoretical scientific communities in recent years [36]. Graphene has a very large specific surface area (2630 m²/g compared to 10 m²/g of graphite and 1315 m²/g of nanotubes), which suggests its high adsorption capacity. The large surface area of graphene can be attributed to its unique nanosheet morphology wherein both surfaces of the planar sheet are accessible for molecular adsorption. Furthermore, the nanosheet structure of graphene is also conducive to fast adsorption equilibrium and analyte elution. The large delocalized π -electron system of graphene can form strong π -stacking interactions with the benzene ring. Thus, graphene may be also a good candidate adsorbent for the adsorption of benzenoid-form compounds.

Graphene has recently been used as the adsorbent for the preconcentration of PAEs [2]. However, graphene is an ultralight material. It is usually hard to retrieve from a suspension even by high-speed centrifugation. As we know, endowing graphene with magnetic properties can solve this problem. Introduction of magnetic properties into graphene will result in a product that combines the high adsorption capacity of graphene and the separation convenience of magnetic materials. Graphene-based magnetic materials were used as the adsorbents for the preconcentration of small molecules [37,38], carbamate pesticides [31], sulfonamide antibiotics [39], triazine herbicides [40], and proteins/peptides [41].

In this work, we synthesized magnetic graphene composites via a simple hydrothermal reaction. The as-prepared composites were applied for the first time as a novel adsorbent for the enrichment and analysis of PAEs using GC–MS. Compared with conventional extraction methods, the proposed technique based on magnetic graphene composites is a simpler, more rapid, more sensitive and more cost-effective method for the extraction of PAEs. Finally, the proposed method was applied in the analysis of real samples including river and pond water.

2. Experimental

2.1. Reagents and materials

A mixture of PAEs standard containing dimethyl phthalate (DMP), diethyl phthalate (DEP), di-*iso*-butyl phthalate (DIBP), di-*n*-butyl phthalate (DBP), di-(2-ethylhexyl) phthalate (DEHP), butylbenzyl phthalate (BBP) and di-*n*-octyl phthalate (DNOP) was purchased from Dr. Ehrenstorfer (Augsburg, Germany). Graphene was purchased from Shanghai Boson Technology Co., Ltd. All other chemicals and reagents were analytical grade. Distilled water was purified by a Milli-Q system (Milford, MA, USA).

The standard solution of PAEs was prepared by diluting the PAEs in acetone with a concentration of 2.0 mg/L. The working standard solution was stored under 4 °C and was found to be stable for 3 months.

To avoid any carryover of PAEs, all laboratory glassware was washed with concentrated hydrochloric acid, and then rinsed with deionized water and acetone, finally dried in the laboratory oven at 100 °C for 1 h. River water samples were obtained from the Xin Jiang River, Shangrao, China. Pond water sample was obtained from our campus. The water samples were stored at 4 °C in glass bottles, and analyzed within one day.

2.2. Synthesis and characterization of magnetic graphene

The magnetic graphene was prepared via a hydrothermal method reported according to the literature method [36] as the following: graphene (400 mg) was dispersed into 50 mL concentrated nitric acid at 60 °C with magnetic stirring for 7 h. The graphene treated by HNO₃ was collected by washing with water for six times and then drying in vacuum at 50 °C. The dried pretreated graphene (150 mg) and FeCl₃·6H₂O (200 mg) were dispersed into 40 mL ethylene glycol solution with trisodium citrate (0.15 g), sodium acetate (1.8 g) and poly(ethylene glycol)-20,000 (1.0 g) by ultrasonication and magnetic stirring for 2 h. The mixture was sealed in the autoclave to be heated at 200 °C for 10 h. Finally the obtained magnetic graphene was washed with water and collected by magnetic separation techniques.

Transmission electron microscopy (TEM) images were taken on a JEOL 2011 microscope (Japan) operating at 200 kV. Scanning electronic microscope (SEM) images were recorded on a Philips XL30 electron microscope (Netherlands) operating at 20 kV.

2.3. Instrumentation

A Focus GC system, coupled with a Thermo DSQ II quadrupole mass spectrometer was used. The extracted compounds were separated using HP-5MS capillary column (30 m × 0.25 mm I.D., 0.25 μ m film). The extraction solvent after MSPE was injected directly in the splitless mode. The oven temperature program was as follows. The initial temperature was 60 °C, and held for 2 min; then increased to 300 °C at a rate of 30 °C/min, and was maintained at 300 °C for 5 min. The injection temperature was 250 °C. Helium (99.999%) was used as the carrier gas with a flow rate of 1.0 mL/min. The quadrupole temperature, transfer line temperature and MS source temperature were 150 °C, 280 °C and 230 °C, respectively. Electron impact ionization (EI) with nominal electron energy of 70 eV was used. The quantitative analysis was carried out in SIM mode. The retention time and ratio of mass-to-charge (m/z) of the characteristic ions for each PAE were presented in Table 1.

2.4. MSPE procedure

MSPE procedure for the extraction of PAEs was as follows: firstly, 10 mL of water sample containing PAEs with a concentration of 100 μ g/L was added in a 10 mL vial with PTFE-silicone septum. Then 20 mg of magnetic graphene composites were added in the vial to extract the analytes, and the mixture was vortexed for 15 min. Next, a magnet bar was placed beside the vial to hold the magnetic graphene composites which had already extracted the analytes. Subsequently the water was removed from the vial with the sorbent remained in the vial. 0.4 mL ethyl acetate and 0.5 g anhydrous Na₂SO₄ were added, and then the mixture was ultrasonicated for 15 min to desorb the analytes. Ethyl acetate was employed to desorb the analytes, and anhydrous Na₂SO₄ was used for removing the residue water. Finally, 0.1 mL of the supernatant was transferred into a 1.5 mL vial, and 1.0 μ L was injected into the GC–MS to analyze.

2.5. Validation of the method

The linearity was investigated by replicating three analyses of the interesting concentration range (0.1–200 μ g/L). The method precision was studied by six replicate analyses of PAEs in water by MSPE under the optimum conditions. The relative standard deviation (RSD) was calculated on the basis of the obtained peak areas. Recovery was also investigated by adding 50 μ L of standard stock solution (10 μ g/mL) to a 10 mL water samples containing known amounts of PAEs. Triplicate measurements were performed

Download English Version:

<https://daneshyari.com/en/article/7613734>

Download Persian Version:

<https://daneshyari.com/article/7613734>

[Daneshyari.com](https://daneshyari.com)