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Graphene nanoplatelets as a highly efficient solid-phase extraction sorbent for determination of phthalate esters in aqueous solution

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ABSTRACT

Graphene nanoplatelet (GN) as a solid-phase extraction (SPE) sorbent in combination with high performance liquid chromatography has been used for the determination of five phthalate esters (PAEs) in aqueous solution. The operation parameters affecting the extraction efficiency were optimized. Comparative studies showed that GN was superior to other common SPE sorbents in terms of recovery and adsorption capacity. Under optimization conditions, detection limits of 0.09–0.33 ng mL^{-1} were achieved for five PAEs and enrichment factors of 402–711 for the analytes were obtained. The proposed method was successfully applied for the determination of PAEs in tap water and drink samples with recoveries ranging from 87.7% to 100.9%.

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1. Introduction

Phthalate esters (PAEs) are widely used as polymer additives in the manufacture of plastics to improve their flexibility and durability [1]. These plastics have been commonly used in the field of food, pharmacy, cosmetics, etc. PAEs themselves are generally stable in the plastics but they can be released from products with time and migrate into environment water, soil, and plants since they are not chemically but only physically bound to the plastics [2]. Due to massive use and persistent character, PAEs have become ubiquitous pollutants in the environment and several PAEs are suspected to be human cancer causing agents and endocrine disruptors. The intensive use of PAEs and their pollutions have become a major public health concern. Several countries have listed PAEs as the priority contaminants [3–5], including U.S. Environmental Protection Agency (EPA) and China [6]. Therefore, it is necessary to develop a simple, sensitive and reliable analytical method for the determination of PAEs.

Very low concentration of PAEs existing in the complicated environmental samples makes sample pretreatment necessary for establishing a reliable determination method for the determination of PAEs prior to chromatographic separation, e.g. the maximum residue level in drinking water for dibutyl phthalate

(DBP) is 3 ng mL^{-1}, which is beyond the detection limit of analytical instruments. To effectively determine such PAEs residue, some sample pretreatment methods were employed for PAEs samples such as liquid–liquid extraction (LLE) [4,7], solid-phase extraction (SPE) [1,8,9], solid-phase microextraction (SPME) [10,11], microwave-assisted extraction (MAE) [12] and so on. Among them, SPE is the most widely used one for environmental samples due to some of its desirable features. The choice of sorbent is a key step to perform SPE successfully. High adsorption capacity and high selectivity are favorable features for a good sorbent. Several kinds of sorbents for SPE have been reported for extraction of PAEs, such as C$_{18}$ [4], polymer [9], bamboo charcoal [6], and multi-walled carbon nanotubes (MWCNTs) [1].

Graphene (G), a novel carbon material with monolayer of carbon atoms densely packed into a two-dimensional honeycomb crystal lattice, has aroused much interests in recent years [13,14]. G has advantages of ultrahigh surface area and high chemical stability. In addition, the large delocalized π-electron structure also endows G a strong affinity for benzene ring-based compounds [15]. These features make it a good candidate for adsorption of benzenoid form compounds. So far, G-related sorbents have been used for extraction of polycyclic aromatic hydrocarbons [16] or chlorophenols [17] or carbamate pesticides [18]. Satisfactory results have been achieved for extraction of above analytes. However, there has been no report that uses G sorbent for extraction of PAEs operated in SPE mode except one report that uses homemade G–Fe$_3$O$_4$ magnetic particles for PAEs [19]. Graphene nanoplate (GN) consisting of multilayers graphene has

been commercially available, which has excellent electrical and thermal performance. Herein we have made attempts to explore the potential of pure GN sorbent-based SPE for the extraction of PAES in aqueous solution. Five widely used PAEs (their structure and other information are provided in Supplementary material, SI-Table 1), including dimethyl phthalate (DMP), diethyl phthalate (DEP), dipropyl phthalate (DPrP), DBP and dicyclohexyl phthalate (DCHP), have been chosen to be the model analytes. The operation parameters affecting the extraction efficiency were optimized. The results showed that GN sorbent was highly effective for extraction of target analytes and was superior to other sorbents.

2. Experimental

2.1. Apparatus and reagents

The chromatographic separation was performed on a Waters 2998 Separations module equipped with a photodiode array detector. A ZORBAX SB-C$_{18}$ column (4.6 mm i.d. × 150 mm length, 5 μm diameter) was used for separation at room temperature. The mobile phase consisting of water (A) and methanol (B) was operated under gradient mode starting from $A/B=50/50$ (v/v) for 10.0 min to $A/B=10/90$ (v/v) for 5 min. The flow rate of the mobile phase was 1 mL/min and the detection wavelength was set at 226 nm. Peak area was used for the measurement of signal intensity.

DMP, DEP, DPrP, DBP and DCHP of analytical grade were supplied by Aladdin (Shanghai, China). HPLC-grade acetonitrile and methanol were purchased from J&K Scientific Ltd. (Beijing, China) and Yuwang Group (Shandong, China), respectively. Four kinds of SPE cartridges containing different sorbents were used for comparison, which included HLB Oasis (5 μm diameter, Waters Corp., USA), C$_{18}$ Silica (5 μm diameter, ~300 m^2/g), Active carbon (http://www.sipore.com/e_cpzs.asp, Sipore Corp., Dalian, China), and MWCNTs (90–120 m^2/g, Shenzhen Nanotech Port Corp., Shenzhen, China). GN with 6–8 nm average thickness and 15 μm average width was purchased from Strem Chemicals Inc. (http://www.strem.com/catalog/v/06–0215/12/carbon_7782-42-5, Massachusetts, USA). The effective specific surface area of GN was measured to be 126 m^2/g, which was close to the value provided by the vendor (120–150 m^2/g). Unless otherwise stated, ultrapure water from Milli-Q system (Millipore, MA, USA) was used for solution preparation.

2.2. SPE operation procedures

30 mg GN was packed in a 1 mL cartridge (6.4 mm i.d., 150 mm height bed, Agilent Corp., USA) and pressed by a glass rod. Two polytetrafluoroethylene (PTFE) frits were set at each end of the cartridge to hold GN in place. The outlet tip of the cartridge was connected to a vacuum pump (Yukang Instrument Corp., Shanghai, China) and the inlet end of the cartridge was connected to the sample solution through a polytetrafluoroethylene (PTFE) suction tube. The operation level of vacuum is controlled to be ~0.06 MPa by a valve. To reduce the possible interference from organic and inorganic contaminants, the entire SPE assembly was carefully washed with sufficient methanol and ultrapure water before its first use.

The SPE operation procedures were as follows. The cartridge was preconditioned with 5 mL methanol and 5 mL ultrapure water prior to each SPE operation. A known volume of ultrapure water spiked with five PAEs was passed through the above preconditioned cartridge at the flow rate of 4 mL/min. The cartridge was then rinsed with 10 mL ultrapure water to remove the residuals. Subsequently the SPE cartridge was eluted with acetonitrile and

the resulting effluent was blown with a gentle N$_2$ flow at room temperature to obtain the residue and then reconstituted to be 1.0 mL. Finally, the extract was analyzed by HPLC with injection volume of 10 μL.

3. Results and discussion

3.1. Evaluation of GN as SPE sorbent

To evaluate the enrichment effect of GN sorbent, five PAEs mentioned above were selected as model analytes. The operation parameters affecting the extraction efficiency, including eluent solvent and its volume, and the sample volume were optimized. For SPE operation, the flow rate of sample loading solution determines the recovery of analytes and the total analysis time. In our experiment, no observable change of the recoveries for five analytes was found when the flow rate of sample loading on the cartridge was up to 4 mL/min. To save analytical time, 4 mL/min of the flow rate of sample loading was chosen in the further experiment.

The eluent solvent for SPE operation has important influence on sample recovery. The choice of eluent solvent is mainly based on the chemical property of the target samples and the chromatographic mode used downstream. Since the separation of five PAEs was performed by reverse phase HPLC (RP-HPLC), the eluent solvent should be compatible with common mobile phase used in RP-HPLC, that is, the eluent solvent should be miscible with the mobile phase. Here five common solvents including acetone, acetonitrile, methanol, ethanol, and methanol/acetonitrile mixture at 50/50 (v/v) were tested. The effect of eluent solvent on the recovery is shown in Fig. 1. It can be seen that acetonitrile is the most effective eluent for five PAEs, probably resulting from strong interaction between acetonitrile and GN due to its property of aprotic solvent. Thus acetonitrile was selected as eluent in the following studies. In addition, the pH effect on the extraction was also explored and it was found that the pH of sample solutions in the range 5.0–8.0 had no significant influence on the recoveries.

To ensure that the model analytes are eluted from the SPE cartridge completely and no carryover occurs, it is necessary to optimize the volume of acetonitrile. The eluent volume in the range of 4–20 mL was tested with 200 mL standard sample solution spiked at 100 ng mL^{-1}. The results are shown in Fig. 2. The recoveries of all PAEs increased with the increase of
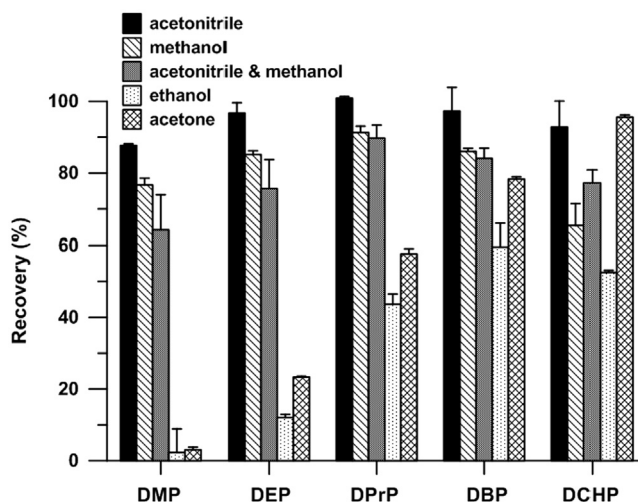

Fig. 1. Effect of eluent solvents on SPE efficiency. Conditions: sample loading volume, 200 mL; concentration of five analytes: 100 ng mL^{-1}; eluent volume, 16 mL. Three replicate measurements for each analyte.