Magnetic graphene oxide for efficient solid phase extraction of DEHP

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Abstract. DEHP (di-2-ethylhexyl phthalate) can cause negative impacts on human health, thus development of reliable analytical methods for the determination of PAEs is important. In this work, magnetic graphene oxide was synthesized and used as the sorbent for solid phase extraction of DEHP. Factors that influence the extraction efficiency of DEHP were studied. The optimum conditions, such as solution pH, extraction time, desorption time, and eluent type and volume were obtained. The analytical performance of the developed method was investigated, and it was found that the limit of detection (LOD) for DEHP was 0.35 μg/L and the related standard deviation (RSD) was 4.3%. The proposed method was applied in the determination of DEHP in environmental water samples with recoveries of 91.6-106.5%.

1. Introduction
Phthalic acid esters (PAEs) are widely used in food packaging materials, personal care products, paints, and building materials. DEHP (di-2-ethylhexyl phthalate) is the most often used one of the PAEs. However, DEHP can cause negative impacts on human health [1-3]. Nowadays, DEHP has been found in various environmental matrices and food samples. Consequently, it is necessary to develop suitable analytical methods for DEHP. Solid-phase extraction (SPE) can be applied for separation and enrichment of pollutants from various matrices, and has been widely used [4-16].

Graphene oxide (GO) is the oxidized derivative of graphene, which has an ultrahigh-specific surface area, superior chemical property and physical stability. Consequently, graphene oxide can be used as the sorbent for SPE [16-22].

Traditional SPE is always a tedious process. However, magnetically separation technology can provide an easy and rapid way for separation of magnetic particles from solution by applying a magnetic field [23-26].

In this work, magnetic graphene oxide was synthesized and used as the sorbent for solid phase extraction of DEHP. Factors that influence the extraction efficiency of DEHP were studied. The optimum conditions, such as solution pH, extraction time, desorption time, and eluent type and volume were obtained. The analytical performance of the developed method was examined. Finally, the developed method was applied for the detection of DEHP in environmental water samples, and satisfactory results were acquired.

2. Materials and methods

2.1. Chemicals
Nature graphite powder (99.95%) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Other chemicals of analytical grade were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China).

2.2. Apparatus
A HPLC system (SHIMADZU, Kyoto, Japan) equipped with diode array detection (DAD, SPD-M20A) and a Shim-pack VP-ODS column (150 x 4.6 mm I.D.) was utilized for analysis. The data obtained were analyzed by the LabSolutions software. A gradient program with a mobile phase system consisting of two parts as eluate A (0.2 M KH$_2$PO$_4$ buffer, pH 2.6) and eluate B (MeOH/ACN 50:50, v/v) was established for the elution of DEHP.

2.3. Preparation of MGO
Graphite oxide (GO) was prepared from nature graphite powders by a modified Hummers method, and magnetic graphite oxide (MGO) was synthesized by a one-pot solvothermal reaction [19].

2.4. Solid phase extraction
50 mg of MGO was added to the 200 mL DEHP containing water sample, and the solution pH was adjusted to pH 7. After shaking for 25 min, the MGO was isolated from solution using a magnetic field. The adsorbed DEHP was eluted with 2 mL of methanol.

3. Results and discussion

3.1. Selection of sample pH
The influence of sample pH on the extraction recovery of DEHP was examined by varying pH value from 4 to 10, and the results were shown in Fig.1. As can be seen, the recovery enhanced with the increase of pH from 4 to 6, and then kept almost unchanged up to pH 8. When the pH value was larger than 9, the recovery decreased. Generally, effect of pH was not great in the pH range of 4-10, and pH 6-8 was optimal.

![Figure 1. Effect of solution pH.](image)

3.2. Selection of extraction time
The effect of extraction time on extraction recovery of DEHP was investigated. As seen from Fig. 2, the recovery increased significantly at the initial adsorption stage from 1 to 15 min. After 25 min, the recovery showed very little changes, indicating the sorption equilibrium was achieved. Based on these results, 25 min extraction time was employed in the subsequent experiments.
3.3. Selection of eluent type and volume
Methanol, acetone and acetonitrile were used as the eluents for stripping of DEHP from the MGO. It was found that methanol gave the highest recovery (97.3%) for DEHP (Fig.3). Thus, methanol was adopted as the eluent solvent. To examine the effect of methanol volume on the extraction recovery of DEHP, different volumes of methanol (1, 2, 3 and 5 mL) were tested. The results indicated that 2 mL of methanol could completely elute the adsorbed DEHP.

3.4. Selection of desorption time
To obtain the optimal desorption time, various time periods were tested in the range of 1 to 20 min. The results were presented in Fig.4. According to Fig.4, 8 min was enough for quantitative elution of DEHP from magnetic graphite oxide.

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**Figure 2.** Effect of extraction time.

**Figure 3.** Effect of eluent type.
3.5 Analytical performance
Under the optimum experimental conditions, the calibration curve of DEHP was linear in the concentration range from 1.0 to 100 μg/L ($R^2=0.9972$). The limit of detection (LOD) for DEHP was 0.35 μg/L. The relative standard deviation (RSD) for 6 replicate measurements of 10.0 μg/L of DEHP was 4.3%.

3.6. Water sample analysis
To evaluate the capability of the proposed method for analysis of practical samples with different matrices containing various amounts of DEHP, three real environmental water samples were analyzed, and the analytical results were given in Table 1. It is obvious that the spiked recoveries of these samples were in the range of 91.6–106.5%, with RSD of 2.3-5.4%. Therefore, the developed method was sensitive, accurate and precise.

| Sample            | Add/(μg/L) | Found/(μg/L) | Recovery(%) | RSD(%) |
|-------------------|------------|--------------|-------------|--------|
| Water sample 1    | 0          | ---          | ---         | 5.4    |
|                   | 5.0        | 4.58         | 91.6        | 3.7    |
| Water sample 2    | 0          | 2.97         | ---         | 3.5    |
|                   | 5.0        | 7.73         | 95.2        | 2.8    |
| Water sample 3    | 0          | 6.42         | ---         | 3.9    |
|                   | 10.0       | 17.07        | 106.5       | 2.3    |

4. Conclusions
Magnetic graphene oxide was synthesized and applied as the sorbent for solid phase extraction of DEHP from solutions. Then a new analytical method for trace detection of DEHP was proposed, using a combination of SPE with HPLC-DAD. Results showed that this method had good performance in terms of limit of detection, linearity, accuracy and reproducibility. The proposed method was used to real environmental water samples, and the obtained recoveries of DEHP were in the range of 91.6–106.5%.
with RSDs of 2.3-5.4%, indicating the suitability of the developed method, due to its sensitivity, rapidity, and reliability.

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