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Dispersive solid-phase microextraction with graphene oxide based molecularly imprinted polymers for determining bis(2-ethylhexyl) phthalate in environmental water

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ABSTRACT

A novel graphene oxide-molecularly imprinted polymers (GO-MIPs) was prepared and applied for selective extraction and preconcentration of bis(2-ethylhexyl) phthalate (DEHP) in environmental water samples by using the dispersive solid-phase microextraction (DSPME) method. The GO-MIPs was synthesized via precipitation polymerization using GO, DEHP, methacrylic acid, and ethylene dimethacrylate as supporting materials, template molecules, functional monomer, and cross-linker, respectively. The prepared GO-MIPs were characterized by scanning electron microscope and Fourier transform infrared spectroscopy. The GO-MIPs-DSPME conditions including type and volume of elution solvents, adsorbents amount, initial concentration of DEHP, pH and ionic strength of water samples were investigated. Under optimized conditions, the DEHP was selectively and effectively extracted in real water samples and enrichment factors of over 100-fold were achieved. Good linearity was obtained with correlation coefficients (R^2) over 0.999 and the detection limit (S/N = 3) was 0.92 ng mL^{-1}. The average recoveries of the spiked samples at three concentration levels of DEHP ranged from 82% to 92% with the relative standard deviations less than 6.7%. The results indicated that the proposed GO-MIPs-DSPME extraction protocol combined with HPLC-UV determination could be applied for selective and sensitive analysis of trace DEHP phthalate in environmental water samples.

1. Introduction

Bis(2-ethylhexyl) phthalate (DEHP), one of the most popular phthalates esters (PAEs) plasticizers, is widely used as plasticizer of common packaging materials such as plastics and rubber to promote their stability and flexibility through weak secondary molecular interactions with polymer chains [1–4]. Because it is physically bound to the polymer chains, it becomes easily released and enters into the environment, and further poses the adverse effects on human health as the suspected endocrine disrupters or mutagens even at low levels [5–8]. Therefore, development of the analytical techniques to efficiently enrich and analyze DEHP in aqueous matrices is essential for extensive surveys on their occurrence and fate in the environment. Conventional sample pretreatment techniques such as liquid–liquid extraction (LLE) and solid phase extraction (SPE) prior to chromatographic determination have been widely used for extraction and preconcentration of the phthalates in environmental samples [9,10]. While reliable, these methods have several shortcomings such as low selectivity and limited enrichment factors. Moreover, the use of large volumes of organic solvents gives rise to large amounts of organic wastes, resulting in environmental and safety concerns.

Molecularly imprinted polymers (MIPs) were increasingly developed to meet the need of selective extraction of target analytes from the complicated sample matrix by its molecular recognition properties. This molecular recognition excellence has been very attractive in many different fields, such as sensors, enantiomeric separations, biomedical and analytical applications [11]. A number of papers published in the past decades reported that MIPs had been successfully applied in SPE as sorbents to extract organic pollutants in environmental waters prior to instrumental analysis [12–14,28,29]. Such approaches usually led to good selectivity and reproducibility. On the other hand, a large number of microextraction methods, such as liquid-phase microextraction (LPME), solid-phase microextraction (SPME), and single drop microextraction (SDME), which are more sensitive, cost-effective

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and environmentally friendly compared to conventional extraction methods, have been successfully developed for the extraction of trace pollutants from a variety of environmental samples [15–17]. Since these techniques are surface dependent processes, dispersive microextraction techniques including of dispersive liquid-phase microextraction (DLPME) and dispersive solid-phase microextraction (DSPME) were recently proposed by means of dispersion to improve the contact area between sample solution and extractants, and further shorten the extraction time and decrease the extractants consumption [18–20]. The key to those techniques is the use of highly efficient extractants media in order to maintain or even improve the preconcentration of the analytes using only a few milligrams or microliters of extractants. Updated developments in this field are mainly related to the use of new sorbent materials with high surface area as extractants [21]. Recently, graphene has received much attention from environmental and analytical scientists ever since their discovery due to its unique mechanical properties and extremely large surface area with two-dimensional structure [22]. Graphene derivatives such as graphene oxide (GO) have been applied to synthesize hydrophilic materials to become water-compatible for various application by modifying with hydrophilic functional groups such as −COOH and −OH [23–25]. Theoretically, compared to general MIPs, the prepared MIPs situated at the large surface of GO could provide higher loading capacity, accelerate association/dissociation kinetics and adsorption, improve the accessibility and sensitivity to target species, and effectively avoid the polymers from caking [26]. Moreover, the extraction efficiency could be further dramatically enhanced by employing the DSPME method with GO-MIPs as extractants. However, little information on the application of GO-MIPs-DSPME for the extraction of pollutants in environmental samples is available.

In the present study, our aims were: (i) to prepare and characterize the GO-MIPs adsorbents for selective extraction of DEHP in aqueous solution; (ii) to investigate the procedures of the GO-MIPs-DSPME method for preconcentration of the DEHP in aqueous samples; (iii) to optimize the variables involved in the GO-MIPs-DSPME process such as type and volume of desorption solvent, amount of consumed GO-MIPs, pH and ionic strength of sample solution; and (iv) to apply the validated GO-MIPs-DSPME-HPLC-UV method to extract and determine the ultra-trace DEHP in real natural water samples.

2. Experiments

2.1. Materials and reagents

Bis(2-ethylhexyl) phthalate (DEHP, >98.0%), methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA, 97.0%) were supplied by TCI chemicals (Tokyo, Japan). 2,2′-Azobis(2-methylpropionitrile) (AIBN) and graphite powder (99.95% metals basis, 5000 meshes) were obtained from Aladdin Reagent Co., Ltd. (Shanghai, China). HPLC grade methanol were supplied by Tjshield chemicals (Tianjin, China). Diphosphorus pentaoxide (P_2O_5), potassium persulfate ($K_2S_2O_8$), sulfic acid (H_2SO_4), potassium permanganate ($KMnO_4$) and acetonitrile (ACN, ≥ 99.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Acetone (≥99.0%) was purchased from Juhua chemicals (Quzhou, China). The AIBN reagents were refined freshly before used by following procedures: 100 mL methanol were heated at 60 °C in a 200 mL beaker until boiling, then added 10 g of original AIBN into the beaker and stirred the solution to make AIBN quickly dissolved. After filtration, the collected solution was recycled in a beaker followed by cooling crystallization in refrigerator overnight. The refined AIBN crystal was dried in vacuum after filtration and showed uniform crystal shape. All other reagents were analytical grade and were used as received. De-ionized water was used throughout the experiments.

2.2. HPLC analysis

The DEHP in standards and water samples were determined by WUFENG LC-100 high-performance liquid chromatograph (Shanghai, China) equipped with a double pump and ultraviolet detector. The chromatographic separations were carried out on a Waters Symmetry C_{18} column (3.9 × 150 mm, 5 μm) at 30 °C by using an isocratic elution program of mobile phase (methanol) at a flow rate of 1.0 mL min^{-1}. Aliquots of 20 μL were injected into the HPLC system, and the detection wavelength was set at 235 nm. All quantification was performed by the external calibration method based on peak areas. Calibration curve was constructed by linear regression of the peak area of standard versus the concentration.

2.3. Preparation and characterization of GO-MIPs adsorbents

2.3.1. Preparation of graphene oxides (GO)

Graphene oxides were prepared by Hummers' method [26] with some modification as following: 60 mL of concentrated H_2SO_4, 1.2 g of $K_2S_2O_8$ and 2.5 g of P_2O_5 were added into a 150 mL three-necked flask and mixed with the aid of magnetic stirring bar. Then 3 g of graphite was slowly added and dispersed into the reaction solution and the mixture kept for 6 h at 80 °C. Afterwards, the mixture solution was immediately poured into 800 mL of purified ice-water and placed on the lab batch overnight at room temperature. After removal of the supernatant, the graphite oxide precipitates were washed with deionized water until the pH of eluted water became neutral and then dried in vacuum freezing drier. The dried graphite oxide was subsequently mixed with 60 mL of concentrated H_2SO_4 in a 150 mL three-necked flask with mechanical stirring in ice-water bath. And 4.0 g of $KMnO_4$ was slowly added into the mixture solution and kept at 60 °C for 10 h. Then the mixture solution was poured into 800 mL of purified ice-water, and the residual $KMnO_4$ and MnO_2 were removed by adding 30% H_2O_2 and 1.0 M HCl solutions, respectively. Finally, the graphene oxide liquid crystals were washed with deionized water until the pH of eluted solution became neutral.

2.3.2. Preparation of GO-MIPs adsorbents

Prior to preparation of GO-MIPs, GO water mixture was centrifuged at 12000 rpm for 10 mins and the water supernatant was decanted, and then GO solids were washed with ACN solvents twice to make GO completely dispersed into ACN solvents. The GO-MIPs was prepared by precipitation polymerization as follows: GO-ACN mixture solution (4.0 mL), ACN (100 mL) and methanol (20.0 mL) were mixed in a 250 mL of three-necked flask, and DEHP (1 mmol) and MAA (4 mmol) were added into the mixture solutions with the stirring by magnetic bar and kept for 2 h. After removal of the dissolved-oxygen by high purity nitrogen gas blowing, the cross-linking agent EGDMA (20 mmol) and the initiation reagents AIBN (50 mg) were added into the solution and sonicated for 10 min to fully dissolve. The polymerization was performed at 65 °C for 6 h in oil bath. Postsynthesis, the polymeric particulates were freed from template and residual monomers via Soxhlet extraction by using methanol, and then the products were dried to constant mass under vacuum at −50 °C in a freeze vacuum drier. To verify that the affinity to analytes was due to molecular recognition but not just to nonspecific binding, and that the adsorption capability of analytes to adsorbents was enhanced by combining GO with MIPs, GO-NIPs (GO non-imprinted polymers), MIPs, NIPs were synthesized as the