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Reduced graphene oxide-coated magnetic-nanoparticles as sorbent for the determination of phthalates in environmental samples by micro-dispersive solid-phase extraction followed by ultra-high-performance liquid chromatography tandem mass spectrometry

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ABSTRACT

In this work, the suitability of Fe_3O_4 nanoparticles coated with reduced-graphene oxide as sorbent was evaluated for the extraction of a group of fourteen phthalic acid esters (i.e. benzylbutyl phthalate (BBP), bis-2-*n*-butoxyethyl phthalate (DBEP), dibutyl phthalate (DBP), diisobutyl phthalate (DIBP), dicyclohexyl phthalate (DCHP), bis-2-ethoxyethyl phthalate (DEEP), diisodecyl phthalate (DIDP), diisononyl phthalate (DINP), bis-isopentyl phthalate (DIPP), bis-(2-methoxyethyl) phthalate (DMEP), dimethyl phthalate (DMP), di-*n*-octyl phthalate (DNOP), bis-*n*-pentyl phthalate (DNPP), dipropyl phthalate (DPP)) from environmental samples. Extraction was carried out using magnetic-micro dispersive solid-phase extraction while separation, identification and quantification of the target analytes were achieved by ultra-high-performance liquid chromatography coupled to triple quadrupole tandem mass spectrometry. The methodology was validated for three different types of water samples using dibutyl phthalate-3,4,5,6-d_4 as internal standard for all of them. Recovery values ranged from 70 to 120% for the three matrices with relative standard deviation values lower than 20%. Limits of quantification of the method achieved were in the range 6–178 ng/L for all samples and analytes. The methodology was applied for the evaluation of real samples finding the presence of DMP, DPP, BBP, DIBP and DBP in some of the analysed matrices.

Abbreviations: ACN, acetonitrile; BBP, benzylbutyl phthalate; DBEP, bis-2-*n*-butoxyethyl phthalate; DBP, dibutyl phthalate; DBP-d_4, dibutyl phthalate-3,4,5,6-d_4; DCHP, dicyclohexyl phthalate; DCM, dichloromethane; DEEP, bis-2-ethoxyethyl phthalate; DEHP, di-(2-ethylhexyl) phthalate; DHP, dihexyl phthalate; DIBP, diisobutyl phthalate; DIDP, diisodecyl phthalate; DINP, diisononyl phthalate; DIPP, bis-isopentyl phthalate; DMEP, bis-(2-methoxyethyl) phthalate; DMP, dimethyl phthalate; DNOP, di-*n*-octyl phthalate; DNPP, bis-*n*-pentyl phthalate; DPP, dipropyl phthalate; dSPE, dispersive solid-phase extraction; EDC, endocrine disrupting chemical; EPA, US Environmental Protection Agency; ESI, electrospray ionisation; EU, European Union; FDA, US Food and Drug Administration; FTN, flow-through needle; GC, gas chromatography; GO, graphene oxide; HPLC, high-performance liquid chromatography; HRTEM, high-resolution transmission electron microscopy; IS, internal standard; LC, liquid chromatography; LCL, lowest calibration level; LPME, liquid-phase microextraction; m-μ-dSPE, magnetic-micro dispersive solid-phase extraction; ME, matrix effect; MeOH, methanol; m-NPs, magnetic-nanoparticles; MRM, multiple reaction monitoring; MS, mass spectrometry; PAEs, phthalic acid esters; QqQ, triple quadrupole; R^2, determination coefficient; r-GO, reduced-graphene oxide; SBSE, stir-bar sorptive extraction; SPE, solid-phase extraction; SPME, solid-phase microextraction; TEM, transmission electron microscopy; UHPLC, ultra-high-performance liquid chromatography; XPS, X-ray photo-electron spectroscopy.

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1. Introduction

The presence of phthalic acid esters (PAEs) in the environment is an issue of special concern, not only from an ecological point of view, but also due to their role as endocrine disrupting chemicals (EDCs) [1–4]. As a result of the known negative effects that these analytes produce on the human's health, the US Environmental Protection Agency (EPA) has included certain PAEs such as dibutyl phthalate (DBP), diisobutyl phthalate (DIBP), benzylbutyl phthalate (BBP), bis-*n*-pentyl phthalate (DNPP), di-(2-ethylhexyl) phthalate (DEHP), di-*n*-octyl phthalate (DNOP), diisononyl phthalate (DINP) and diisodecyl phthalate (DIDP) as priority substances whose use should be addresses. Furthermore, the European Union (EU) has listed bis-(2-methoxyethyl) phthalate (DMEP), DEHP, DBP, bis-isopentyl phthalate (DIPP), BBP [5] DIBP [6], DNPP [7] and dihexyl phthalate (DHP) [8] as substances with reproductive toxicity. However, despite the interest of the scientific community and regulatory organisations, the legislation regarding the presence of these compounds in environmental media and particularly in water samples is still insufficient. In fact, only EPA and the US Food and Drug Administration (FDA) have established a maximum concentration limit for DEHP in bottled water at 6 μg/L [9] but not for other types of water and PAEs, probably due to the lack of knowledge about the risk-assessment of this kind of compounds on health [4]. Besides, the EU in one of the last resolutions published on this respect [10], highlighted that there was no scientific basis for setting a limit value for EDCs, since they have an effect even at extremely low concentrations. Additionally, the ubiquitous presence of PAEs in the environment hinders the efficient application of methodologies and, consequently, their analysis. For this reason, the development of sensitive and selective procedures that allow the monitoring of phthalates in these environmental samples are of special interest in order to effectively evaluate the exposition of the population to these contaminants.

Different techniques have been applied for the extraction of PAEs from water samples. Among them, liquid-phase microextraction (LPME) techniques, solid-phase microextraction (SPME), stir-bar sorptive extraction (SBSE) and solid-phase extraction (SPE) techniques, in their different approaches, have been the most commonly applied, using or not nanomaterials, in combination with liquid chromatography (LC) and gas chromatography (GC) techniques hyphenated to conventional and mass spectrometry (MS) detectors [11]. Although other alternative procedures like electronic sensors have been also used with this aim [4].

The application of nanomaterials as extraction sorbents has sharply increased in the last years due to the numerous advantages that their use offers in terms of extraction efficiency, simplicity and miniaturisation. Particularly, graphene based materials have been markedly applied since their characteristic structure provides them large surface area, the possibility to be chemically modified, as well as the possibility of establishing π-π interactions, due to its delocalised electrons, that make them excellent sorbents. Apart from that, graphene oxide (GO) and reduced-GO (r-GO) possess important amounts of oxygen atoms on its surface such as epoxy, hydroxyl and carboxyl groups that improve its hydrophilicity favouring their dispersion in aqueous media and additionally allow them establishing hydrogen bonds or electrostatic interactions with diverse compounds, which enhance the specificity of the extraction process [12,13]. Furthermore, their combination with magnetic-nanoparticles (m-NPs) has been also widely applied since, the possibility of a rapid separation of the sorbent by the use of an external magnetic field; considerably simplifies the procedure [14–17].

Despite the output that the use of r-GO offers in the extraction of organic compounds and the advantages respect to GO, associated with the higher hydrophobic p-conjugated carbon atoms that are prone to interact with the delocalized electrons of the aromatic rings common for PAEs structures [18], only a few publications have reported the application of this sorbent for the extraction of such compounds from river and lake [19,20] as well as drinking bottled water [20,21]. In these cases the nanomaterial has been applied both for the coating of a Ti SPME fibre [21], using a cross-linking agent, and as sorbent, combined with aminosilica nanoparticles, in dispersive solid phase extraction (dSPE) [19]. However, their combination with m-NPs such as Fe_3O_4 has only been reported in one occasion for the extraction of a reduced number of PAEs from water samples [20].

Taking into account the above mention, the aim of this work is to develop a new methodology based on the use of a Fe_3O_4@r-GO nanomaterial, synthesised and characterised in our laboratory, as sorbent for the magnetic-micro dispersive solid-phase extraction (m-μ-dSPE) of fourteen phthalic acid esters (i.e. BBP, bis-2-*n*-butoxyethyl phthalate (DBEP), DBP, DIBP, dicyclohexyl phthalate (DCHP), bis-2-ethoxyethyl phthalate (DEEP), DIDP, DINP, DIPP, DMEP, dimethyl phthalate (DMP), DNOP, DNPP, dipropyl phthalate (DPP)) from mineral, pond and wastewater prior their determination by ultra-high-performance liquid chromatography-triple quadrupole-tandem MS (UHPLC-QqQ-MS/MS). To the best of our knowledge, this work constitutes the first time in which this kind of sorbent has been applied for the evaluation of the group of fourteen PAEs included in this study from water samples prior their determination by UHPLC-QqQ-MS/MS.

2. Experimental

2.1. Chemicals and materials

Analytical standards of DBP (CAS 84-74-2), dibutyl phthalate-3,4,5,6-d_4 (DBP-d_4) (CAS 93952-11-5), DCHP (CAS 84-61-7), DIDP (CAS 26761-40-0), DINP (CAS 28553-12-0), DMEP (CAS 117-82-8), DNOP (CAS 117-84-0), DPP (CAS 131-16-8) from Sigma-Aldrich Chemie (Madrid, Spain) and BBP (CAS 85-68-7), DBEP (CAS 117-83-9), DEEP (CAS 605-54-9), DIBP (CAS 84-69-5), DIPP (CAS 605-50-5), DMP (CAS 131-11-3), DNPP (CAS 131-18-0) from Dr. Ehrenstorfer GmbH (Augsburg, Germany) were used without further purification (purity $\geq$ 97%).

Individual stock solutions of each analyte were prepared in acetonitrile (ACN) at 70 mg/L for DBP-d_4; 100 mg/L for DMEP, DBEP and DINP; 500 mg/L for DEEP, DPP, BBP, DIBP, DBP, DNPP, DCHP, DNOP and DIDP and 1000 mg/L for DMP and DIPP and stored in the darkness at -18 °C. Working analyte mixtures were daily prepared by dilution with the appropriate volume of initial mobile phase.

All chemicals were of analytical reagent grade (unless otherwise indicated) and used as received. ACN and methanol (MeOH) of high-performance liquid chromatography (HPLC)-MS grade, cyclohexane of GC-MS grade and hydrochloric acid (25%, w/w) were from Merck (Darmstadt, Germany). Ammonium hydroxide; hydrazine hydrate, hydrogen peroxide (30% w/w), potassium permanganate, sodium nitrate, and iron (II) chloride tetrahydrate were from Sigma-Aldrich Chemie (Madrid, Spain). Formic acid and sulfuric acid were from Panreac Química S.L.U. (Barcelona, Spain). Dichloromethane (DCM) and ethanol of HPLC grade as well as iron (III) chloride hexahydrate from Scharlau Chemie S.A. (Barcelona, Spain). Water was deionised by a Milli-Q gradient system A10 from Millipore (Bedford, MA, USA).

With the aim to guarantee the absence of PAEs contamination in the laboratory material, non-volumetric glassware was calcined at 550 °C during 4 h whereas Nochromix® (prepared as indicated by the manufacturer) from Godax Laboratories (Maryland, USA) was used to clean the volumetric glassware. Furthermore, PAEs free

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