



# Magnetic nanoparticles coated with ionic liquid for the extraction of endocrine disrupting compounds from waters



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## ABSTRACT

A hybrid nanomaterial was synthesized to be used in dispersive solid phase microextraction. It consist of a magnetic core ( $\text{Fe}_3\text{O}_4$ ), obtained by coprecipitation covered by a silica ( $\text{SiO}_2$ ) layer were the ionic liquid methylimidazolium hexafluorophosphate (MIM- $\text{PF}_6$ ) was attached. The  $\text{Fe}_3\text{O}_4@/\text{SiO}_2@/\text{MIM-}\text{PF}_6$  nanoparticles have been characterized by microscopy and X-ray diffraction. The chemical composition of the hybrid nanoparticles has been studied by infrared spectroscopy and thermogravimetric analyses. Finally, its potential in dispersive microextraction was evaluated for the isolation of 11 endocrine disrupting compounds (benzophenones, bisphenol A and parabens) from water samples.

For this purpose, 10 mg of the  $\text{Fe}_3\text{O}_4@/\text{SiO}_2@/\text{MIM-}\text{PF}_6$  are added to 100 mL of water sample ( $\text{pH} = 8$ , NaCl 30% w/v) dispersed by ultrasound (1 min) and vortex stirring (20 min). Next, an external magnet is used to recover the MNPs. Later, the analytes are eluted from MNPs with 500  $\mu\text{L}$  of methanol under ultrasonic irradiation. 5  $\mu\text{L}$  of the extract is finally injected into a liquid chromatograph with tandem mass spectrometric detection (HPLC-MS/MS) for analytes separation and quantification.

The proposed microextraction method allows the determination of the target compounds with limits of detection in the range from 0.16 to 1.21  $\mu\text{g/L}$  and the linearity was maintained between the limits of quantification and 500  $\mu\text{g/L}$ . The precision, expressed as relative standard deviation was better than 8.3%. The recovery study was performed on different water samples obtaining percentages higher than 87%, which demonstrated the applicability of the hybrid sorbent for the selected analytical problem. Moreover, the proposed method provides enrichment factors in the range from 15.4 to 49.2. Butylparaben, benzophenone 3 and benzophenone 6 were detected in the swimming pool water samples analyzed following the proposed microextraction method. The simultaneous presence of analytes from different endocrine disrupting families reveal the need for methodologies including a wider variety of compounds than those currently available.

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## 1. Introduction

Endocrine disrupting chemicals (EDs) are a group of natural and synthetic compounds that may interfere with the normal function of the endocrine system in animals and humans; producing several adverse effects [1]. Therefore, there is growing concern about negative human health and environmental impacts possibly caused by endocrine disrupters. The European Union and Environmental Protection Agency have introduced specific legislative obligations aimed at phasing out endocrine disrupters in water, industrial chemicals, plant protection products and biocides [2]. The term EDs define a heterogeneous group of chemical compounds [3], including benzophenones (BPs), bisphenol A (BPA) and parabens (PBs). The common use of several personal care

products nowadays makes necessary the development of analytical methods able to simultaneously detect different families of compounds in a given sample in order to optimize the time and resources of the laboratories. Taking into account the potential complexity of the matrices, the low concentration of the analytes and the large number of compounds to be determine the combination of (micro)extraction techniques with chromatographic separation is the preferred choice [4–6].

Benzophenones are a family of compounds which are used in the cosmetic industry as UV-filters to protect skin against UV radiation damage. BPs include 12 main compounds (benzophenone-1, to benzophenone-12), and other less known such as 2-hydroxybenzophenone, 3-hydroxybenzophenone and 4-hydroxybenzophenone [7]. The problems associated to the use of these compounds are numerous such as to stimulate cancer proliferation [8,9], or to produce carcinogenesis and reproductive organ malformations [10,11]. Moreover, their degradation compounds can be more dangerous than the parent BPs [12].

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Bisphenol A is an estrogenic disrupting endocrine used in plastic industry to produce polycarbonate plastic products and epoxy resins. Also it can be used as flame retardant in other materials [13]. In addition, this compound is also present in food and beverage containers [14]. As result, BPA can migrate from the package to the food [15].

Parabens are alkyl esters of *p*-hydroxybenzoic acid. These compounds include methylparaben, ethylparaben, propylparaben and butylparaben, which are used as preservatives in pharmaceuticals, cosmetics and food due to their behavior as antimicrobial and antifungal agents. PBs have multiple actions, but their effect as inhibitor on membrane transport and mitochondrial function has been described [16]. However, their potential contribution to the incidence of breast cancer has been highlighted, and for this reason parabens' use in cosmetics is controlled.

Ionic liquids (ILs) have been used as eco-friendly "green" extraction solvents in place of traditional organic ones because of their unique chemical and physical properties, such as negligible vapor pressure, good solubility, and high thermal stability [17,18]. The ILs were used as effective sorbent for separation and preconcentration of several EDs [19,20]. The main disadvantages of IL in microextraction techniques are related to the difficulty of quantitative recovery of the low volume used in these miniaturized formats. In order to overcome these problems, linkage of ILs on suitable supports is desirable.

In this context, ionic liquid coated magnetic nanoparticles (IL-MNPs), have been proposed to take advantage of the synergic combination of both elements, for magnetic solid phase extraction [21–25]. The covalent immobilization provides the ionic liquid coating with a high stability avoiding it losses in the extraction and elution processes, while allows its reuse after a soft cleaning process. Finally, the paramagnetic properties permit the easy sorbent recovery after the extraction by application of an external magnetic field.

In this work, we describe the synthesis of a hybrid nanosorbent combining the properties of MNPs and ILs. These hybrid nanoparticles are composed of a magnetic core ( $\text{Fe}_3\text{O}_4$ ) and an IL (MIM- $\text{PF}_6$ ) coating. In order to preserve the integrity of the core, a  $\text{SiO}_2$  layer was created prior to the immobilization of the ionic liquid. As the analytes selected for this study were endocrine disrupters, methylimidazolium-based IL was selected on account of its better interaction with the target compounds. The  $\text{Fe}_3\text{O}_4@/\text{SiO}_2@/\text{MIM-PF}_6$  (IL-MNPs) resulted to be easily dispersed in water and efficiently removed after analytes interaction by means of an external magnet. The analytical figures of merit of the proposed microextraction procedure were adequate to determine BPs, BPA and PBs in river, sea and swimming pool water samples.

## 2. Materials and methods

### 2.1. Reagents and samples

All reagents were of analytical grade or better. Benzophenone-1, benzophenone-2, benzophenone-3, benzophenone-6, benzophenone-8, 4-hydroxybenzophenone, bisphenol A, methylparaben (methyl-4-hydroxybenzoate), ethylparaben (ethyl-4-hydroxybenzoate), propylparaben (propyl-4-hydroxybenzoate) and butylparaben (butyl-4-hydroxybenzoate) were supplied by Sigma–Aldrich (Madrid, Spain). Stock standard solutions of each analyte were prepared in acetonitrile (Sigma–Aldrich) at a concentration of 1 g/L and stored at 4 °C in the dark. Working standards were prepared on a daily basis by rigorous dilution of the stock in Milli-Q water (Millipore Corp., Madrid, Spain) or acetonitrile as required. In the extraction procedure, sodium chloride (Sigma–Aldrich) was used to adjust the ionic strength and methanol (Sigma–Aldrich) was employed as eluent.

All the reagents required for the synthesis of the magnetic nanoparticles were purchased from Sigma–Aldrich. Ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ), ferrous chloride ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ) and ammonia were used for the synthesis of the magnetic core ( $\text{Fe}_3\text{O}_4$ ). Tetraethylorthosilicate (TEOS) and ethanol were employed for covering the magnetic core with a protective silica-

based coating. Hydrochloric acid, 3-chloropropyltrimethoxysilane, *N*-methylimidazole, triethylamine, potassium hexafluorophosphate ( $\text{KPF}_6$ ) and toluene were used to introduce methylimidazolium hexafluorophosphate (MIM- $\text{PF}_6$ ) functional groups on the nanoparticles surface.

River, sea and swimming pool water samples were collected in amber-glass bottles without headspace. The samples were stored in the dark at 4 °C until their analysis.

### 2.2. Apparatus

Two chromatographic systems, including different detectors, were employed in the development of the present research.

The optimization of the extraction procedure was carried out on a Waters-Acquity™ Ultra Performance LC system (Waters Corp., Madrid, Spain) using an Acquity UPLC® BEH C18 column (1.7  $\mu\text{m}$ , 2.1 mm  $\times$  100 mm) maintained at 60 °C. The mobile phase consisted of (A) water and (B) acetonitrile at a flow rate of 0.4 mL/min using a gradient elution program. The initial composition was fixed at 75% A, the percentage being decreased to 70% in 3 min, then decreased to 50% in 8 min. The injection volume was 5  $\mu\text{L}$  with partial loop with needle overfill injection mode. The separated analytes were determined using a PDA e $\lambda$  (extended wavelength) detector (Waters) at 254 nm. System control was achieved with Empower software.

The validation of the methodology was performed on an Agilent 1260 HPLC system equipped with a pump, a degasser, an autosampler and a thermostated column compartment (Agilent Technologies, Palo Alto, CA, USA). Chromatographic separation was carried out at 40 °C on an Agilent Eclipse XDB-C<sub>18</sub> analytical column (4.6 m  $\times$  150 mm, 5  $\mu\text{m}$ ). The mobile phase comprised 0.05% ammonia formate aqueous solution (solvent A) and acetonitrile (solvent B) at a flow rate of 0.2 mL/min and it was operated under the gradient elution mode. The gradient program was as follows: 0 min, 65% B, 0–10 min, 100% B and back to 65% B in 0.5 min. Equilibration time was fixed in 5 min and 5  $\mu\text{L}$  was selected as injection volume. MS spectra analyses were conducted on an Agilent 6420 triple quadrupole mass spectrometer equipped with electrospray ionization source (Agilent Corporation, MA, USA). Quantification was performed in negative mode using multiple reaction monitoring (MRM). Instrument parameters were as follows: source temperature, 200 °C, cone gas flow, 9 L/min; capillary voltage, 2000 V, nebulizer gas flow, 60 psi and cel accelerator voltage 7 V. Nitrogen (99.995%) was used as cone, desolvation and collision gas. Dwell time was set at 30 ms. Optimized parameters for each compound are also listed together with the mass transitions in Table 1. Data acquisition was performed with MassHunter Workstation (Agilent Technologies, USA).

Infrared spectra were performed in a Bruker Tensor37 FT-IR spectrometer, equipped with a diamond ATR cell with a circular surface of 3 mm diameter and three internal reflections. A Deuterated Triglycine Sulfate (DTGS) detector was used for spectra acquisition. Spectra were collected between 4000 and 500  $\text{cm}^{-1}$  at a 4  $\text{cm}^{-1}$  resolution with 64 coadded scans each. Data collection was made using OPUS software (Bruker, Ettlingen, Germany).

Micrographs of the NPs were obtained in a JEOL JEM 1400 transmission electron microscopy (TEM) and were used to characterize their particle size and morphology.

The thermogravimetric analysis (TGA) curves were registered using a TGA/DSC 1 Star System Mettler Toledo (L'Hospitalet de Llobregat, Barcelona, Spain). MNPs were heated from 25 °C to 1000 °C, at 5 °C  $\text{min}^{-1}$ , in an oxidant atmosphere flowing at 100 mL  $\text{min}^{-1}$ .

X-ray diffraction (XRD) patterns were recorded on a Siemens D5000 X-ray diffractometer, using Cu K $\alpha$  radiation and a graphite monochromator.

A vortex stirrer from IKA® (Staufen, Germany) and a ultrasonic bath (50 W, 40 KHz) from J. P. Selecta (Barcelona, Spain) were also used in the extraction procedure. A neodymium magnet (60 mm  $\times$

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