Recycling polymer residues to synthesize magnetic nanocomposites for dispersive micro-solid phase extraction

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ABSTRACT

The ubiquitous presence of plastics, an obvious consequence of their usefulness and low price, has turned them into a problem of environmental and safety concern. The new plastic economy, an initiative recently launched by the World Economic Forum and Ellen MacArthur Foundation, with analytical support from McKinsey & Company, promotes a change in the use of plastic worldwide around three main pillars: redesign, reusing and recycling. Recycled plastics, with the aim of extending their life spam, can be used to synthesize materials for analytical purposes. In this article polystyrene (PS) trays, previously used for food packaging, are proposed as polymeric source for the synthesis of magnetic nanocomposites. The synthesis plays with the solubility of PS in different solvents in such a way that PS is gelated in the presence of cobalt ferrite nanoparticles which are finally embedded in the polymeric network. The extraction capability of the magnetic PS nanocomposite was evaluated using the determination of four parabens (methylparaben, ethylparaben, propylparaben and butylparaben) in water using liquid chromatography-tandem mass spectrometry as model analytical problem. Under the optimum conditions, limits of detection and quantification were in the range of 0.05–0.15 and 0.15–0.5 ng/mL, respectively. The precisions, expressed as relative standard deviation (RSD), varied between 4.4% and 8.5% and the relative recoveries for analysis of the water samples were in the interval 81.2–104.5%.

1. Introduction

The overall production of plastics worldwide reached 311 millions of tons in 2014 [1], the European Community contribution representing the 20% of this amount. The undoubted usefulness and low price of plastics, that build the world we live in, make these materials ubiquitous. Owing to that, plastics have become a current problem of environmental and safety concern. The pollution of environmental waters with bulk materials (e.g single use plastic bags) [2], fibers [3], plastic residues [4,5] and even plastic additives [6] is periodically reported, having a dramatic effect on the ecosystems. This is also a safety problem for humans whose exposure is further aggravated by the extensive use of plastic containers for food packaging [7]. In the light of the data exposed above, policy-makers have identified this situation as a critical and priority issue. The World Economic Forum and Ellen MacArthur Foundation, with analytical support from McKinsey & Company, promoted the so-called "The new plastics economy" [8] in 2016 to face this global challenge. This initiative has been recently complemented by a new document [9] where specific actions, hinged around three main pillars (namely: redesign, reusing and recycling), are recommended. Analytical Chemistry may play a double role in this complex scenario. As it is obvious, the development of methods able to determine all these compounds in samples of different nature is essential to control these situations indicating the necessity of further actions (e.g. remediation). Complementarily, plastics can be recycled to fabricate new materials with analytical applications.

Polymers are extensively used in analytical laboratories for different purposes including passive (containers, flasks, tubing and filters) and active ones. Among the latters, their potential as sorptive phases in solid phase extraction [10] and solid phase microextraction [11–14] is beyond any doubt. Polymers are versatile thanks to their availability in different compositions and formats (beads, coatings, membranes). Apart from the high commercial availability, some polymer can be ad-hoc synthesized in the lab [15,16] according to the analytical problem under study.

The combination of nanoparticles (NPs) and polymers, forming the

so-called polymeric nanocomposites, expands even more the application scope [17]. Nanocomposites, which merge the properties of both materials, can be synthesized in different ways. On the one hand, the polymer can be attached by electrostatic [18] or covalent [19] interactions to the NPs surface, the resulting composite maintaining the nanometric size. On the other hand, the NPs can be embedded in the micrometric polymeric network [20] modifying the porosity of the structure. Among all the combinations, magnetic nanocomposites are the preferred option in dispersive micro-solid phase extraction thanks to their easy dispersion and retrieval applying an external magnetic field [21,22].

In 2016, Psillakis et al. demonstrated the potential of industrial plastic pellets as sorptive phases towards polycyclic aromatic hydrocarbons opening a door to use plastic overstock in a different way [23]. The present article delves into this idea proposing the recycling of polystyrene (PS) into nanocomposite to extend the usable life of the plastic. PS, which is widely employed for food packaging among other uses, presents a very slow degradation rates in the environment [24]. Its expandable form, as that use in this work, causes outsized troubles when they leak into marine environments and contaminate water [25]. The synthesis of the magnetic nanocomposite is based on the different solubility of the polymer in two solvents following a workflow that has been successfully used by our group on the synthesis of polyamides-based nanocomposites [26,27]. In short, the polymer is dissolved in an appropriate solvent and a defined amount of magnetic NPs (MNPs) are dispersed into this solution. The dispersion is finally injected in a different medium which induces the precipitation of PS around the MNPs. The synthesized nanocomposite has been completely characterized and practically evaluated for the extraction of selected parabens from water samples.

2. Experimental section

2.1. Reagents

All the reagents were of analytical grade or better. Unless otherwise specified, they were purchased from Sigma-Aldrich (Madrid, Spain). Stock standards solutions of the analytes (methylparaben, ethylparaben, propylparaben and butylparaben) were prepared in acetonitrile at a concentration of 1000 μg/mL. These solutions were stored at 4 °C in the dark until being used. Working solutions were prepared daily by rigorous dilution of the stocks in methanol or Milli-Q water (Millipore Corp., Madrid, Spain) as required.

Iron(III) nitrate nonahydrate, cobalt(II) nitrate hexahydrate, sodium hydroxide and hydrogen peroxide (33% v/v) were employed for the synthesis of the magnetic nanoparticles (Fe_2CoO_4). Commercial PS trays, previously used for food packaging, were used as polymer source. Chloroform and acetone were selected as solvents to induce the solubilization/precipitation of PS which is essential in the synthesis of the magnetic nanocomposite.

2.2. Synthesis of the magnetic polystyrene nanocomposite

MNPs were synthesized using iron(III) nitrate nonahydrate (20.2 g) and cobalt(II) nitrate hexahydrate (7.3 g) as precursors. These compounds were firstly dissolved in 50 mL of Milli-Q water, the solution being heated at 80 °C. After that, 250 mL of a sodium hydroxide solution (1.2 M) was added dropwise, maintaining the reaction mixture under vigorous stirring for 2 h at the same temperature. Finally, 250 mL of hydrogen peroxide (33% v/v) was gradually added, the resulting dispersion being in continuous stirring for 2 h. As a result of this process, Fe_2CoO_4 MNPs were obtained. These MNPs were isolated by using an external magnet, rinsed with Milli-Q water and acetonitrile, and finally dried in an oven at 80 °C.

Commercial PS trays were manually ground to favor the preliminary washing of the polymer (water and acetone) and its final dissolu-

tion. The polymer (150 mg) was dissolved in chloroform (5 mL) and 200 mg of MNPs were dispersed into solution aided by ultrasounds (5 min). The dispersion was added over acetone (50 mL) by a glass dropper. The solvent changeover, from chloroform to acetone, reduces dramatically the solubility of PS inducing its gelation around MNPs. The final magnetic PS nanocomposite was washed and dried in a oven before being used.

2.3. Characterization of the magnetic polystyrene nanocomposite

The magnetic PS nanocomposite was characterized using several instrumental techniques aimed at knowing its chemical composition (infrared spectroscopy and elemental analysis) and morphology (microscopy and superficial area measurements).

Fourier transform infrared (FT-IR) spectra were recorded with a Bruker Tensor 37 FT-IR spectrometer, equipped with a diamond ATR cell with a circular surface of 3 mm diameter and three internal reflections. The spectrometer has a Deuterated Triglycine Sulfate (DTGS) detector for spectra acquisition. The measurements were performed in the range of 600–4000 cm^{-1} at a 4 cm^{-1} resolution with 64 coadded scans. Data collection was carried out using OPUS software (Bruker, Ettligen, Germany). Carbon content of the synthesized composites was measured by a EuroVector Elemental Analyzer EA3000 (EuroVector SpA, Milan, Italy).

Scanning electron microscopy (SEM) images of the synthesized composite were obtained using a JEOL JSM 6300 scanning electron microscope while the superficial area of the materials was measured in a Quantachrome® ASiQwinTM-Automated Gas Sorption Data analyzer. The measurements were based on the nitrogen adsorption/desorption at −196 °C and BET (Brunauer–Emmett–Teller) equation was used for calculation of the specific surface area values.

Both the micrographs and elemental analysis were developed in the Central Service for Research Support (SCAI) of the University of Cordoba. Gas sorption measurements were played out in the Institute of Fine Chemistry and Nanochemistry at the University of Cordoba.

2.4. Extraction procedure

The dispersive micro-solid phase extraction involves several and well defined steps. First of all, 40 mg of the magnetic PS nanocomposite is placed in a 25 mL glass vial and 1 mL of methanol is added for sorbent conditioning. After that, Milli-Q water at pH 3 is added for sorbent equilibration followed by the addition of 20 mL of aqueous standard or sample adjusted at pH 3. The vial, containing both the sorbent and the sample, is agitated in a vortex for 15 min to enhance the transference of the analytes from the bulk solution to the nanocomposite. The use of multiport vortex allows the simultaneous extraction of several samples. After the extraction, the nanocomposite is washed with 5 mL of Milli-Q water, dried and eluted with 500 μL of methanol. The final eluate is evaporated to dryness in a multiport vacuum concentrator and the residue is dissolved in 50 μL of methanol for further instrumental analysis. The above described procedure takes advantage of the magnetic nature of sorbent in such a way that the nanocomposite is easily recovered from the working solution (solvent, standard or sample) by an external magnet (549.4 N of maximum magnetic force, Supermagnete, Gottmadingen, Germany).

2.5. LC-MS/MS analysis

Liquid chromatographic analyses were carried out by an Agilent 1260 Infinity HPLC system (Agilent, Palo Alto, CA, USA) equipped with an autosampler and a binary high-pressure pump for mobile phase delivery. Separation was performed on a Poroshell 120 SB-C18 column (2.7 μm, 2.1 mm×75 mm) from Agilent, under a gradient elution program using water (solvent A) and acetonitrile (solvent B) as mobile phase components. The gradient elution program was as follows: 30%