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Plastic pellets sorptive extraction: Low-cost, rapid and efficient extraction of polycyclic aromatic hydrocarbons from environmental waters☆

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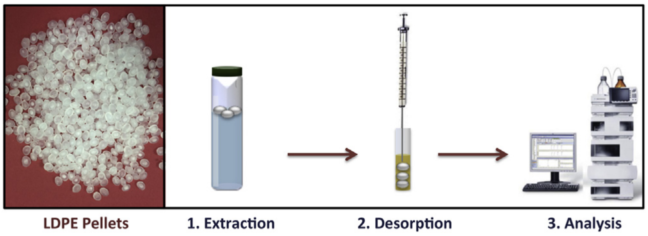
HIGHLIGHTS

- Plastic pellets used as a low-cost and easy to reach sorbent material for the laboratory extraction of PAHs.
- Two step sorptive extraction: adsorption to pellets followed by desorption to organic solvent.
- Very good sensitivity achieved within very short sampling times due to vortex agitation.

GRAPHICAL ABSTRACT



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ABSTRACT

For the first time, plastic pellets, a low-cost and easy to reach industrial raw material, are reported as an efficient sorbent material for the laboratory extraction of polycyclic aromatic hydrocarbons (PAHs) from environmental waters. The proposed methodology, termed plastic pellets sorptive extraction (P2SE), consisted of a two-step procedure whereby target analytes were initially adsorbed onto the surface of three low-density polyethylene (LDPE) pellets and then desorbed using microliters of an organic solvent. Interphase mass transfer was greatly accelerated by means of vortex agitation. Organic extracts were analyzed by means of liquid chromatography-fluorescence detection. Different experimental parameters were controlled and the optimum conditions found were: three LDPE pellets (~80 mg) added to 20 mL aqueous sample (20% w:v NaCl) followed by vortex agitation at 3000 rpm; for desorption, the three LDPE pellets were immersed in 100 μL of acetonitrile and the mixture was shaken at 3000 rpm for 5 min using the vortex agitator. The calculated calibration curves gave high levels of linearity yielding coefficients of determination (r^2) greater than 0.9913. The precision of the proposed method was found to be good and the limits of the detection were calculated in the low ng L^{-1} level. Matrix effects were determined by applying the proposed method to spiked river water, treated municipal wastewater and seawater samples. To compensate for the low recoveries of the more hydrophobic PAHs in spiked effluent wastewater and seawater samples the standard addition methodology was applied. The proposed method was applied to the determination of target pollutants in real seawater samples using the standard addition method. Overall, the performance of the proposed P2SE method suggests that the use of inexpensive and easy to reach sorbent materials for extracting analytes in the laboratory merits more intensive investigation.

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1. Introduction

During the past two decades, efforts have increasingly been devoted to the development of simpler, faster, and more

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sustainable sample preparation methods, with focus on miniaturization, reduction, or elimination of organic solvent and automation to enable higher throughput [1]. Admittedly, solid-phase microextraction (SPME) established the basis for the development of many such techniques, all sharing the same principle, *i.e.*, equilibrium partitioning of the analytes between the sample and a small amount of an acceptor phase [1–3]. In an attempt to overcome the limitations inherent to the SPME fiber approach, different new sorbent-based extraction techniques were reported. For example, to address the limitation of low distribution coefficients of some analytes between the SPME fiber and matrix, polydimethylsiloxane (PDMS)-based stir-bar sorptive extraction (SBSE) [4] and thin-film microextraction (TFME) methods [5] were recently proposed offering larger extraction phase volumes and resulting in considerably higher efficiencies than the SPME fiber approach. At the same time, the introduction of new sorbent materials resulted in improved selectivity, increased sorptive capacity (and therefore sensitivity), or enhanced thermal, chemical or mechanical stability over existing sorbent materials [3]. By way of illustration, to overcome the low extraction efficiency of PDMS for polar compounds new materials (such as monolithic materials [6], molecularly imprinted polymers [7], restricted access materials [8], polyurethane foams [9] and mixed phase TFME coatings [1]) were previously reported.

A less explored direction of sorbent-based extraction techniques focuses on the evaluation of inexpensive and easy to reach sorbent materials that meet the analytical requirements of purity, inertness and, depending on the application, thermal stability. Owing to their low cost, they are generally considered as single-use disposable sorbents, avoiding thus carry-over problems and changes in the extraction efficiency due to chemical/mechanical deterioration [2,10]. Popp et al. proposed the use of commercially available silicon materials (in the form of rods and tubes), as a low-cost alternative to stir bars [11]. They were initially applied to the extraction of polycyclic aromatic hydrocarbons (PAHs) from water and then to a variety of organic contaminants and in different sampling modes [12]. In another report, Prieto et al. compared the performance of commercially available polyethersulphone (PES) tube, polypropylene (PP) tube and Kevlar multi-filament yarn to that of PDMS rod and larger extraction yields (for both polar and non-polar compounds) and reported lower matrix effects when using PES [10]. Finally, the efficiency of four commercially available and low-cost polymeric materials (PP, poly(ethylene terephthalate), Raffia, and PES) for the simultaneous extraction of 16 organic compounds from environmental water samples was recently evaluated [2].

The ability of "marine" plastic debris to adsorb hydrophobic organic compounds from seawater and the use of polymeric materials as passive samplers led scientists to measure persistent organic pollutants (POPs) on recovered plastic debris [13]. To this end, plastic preproduction pellets, a recognizable component of marine debris, have been used to establish a global association between POPs and plastic debris collected from coastal and oceanic waters [13–15]. Plastic pellets are small granules used as an industrial raw material for the plastic industry and can be unintentionally released to the environment both during manufacturing and transport [14]. The physical and chemical properties of plastic pellets influence sorption of chemicals, though polymer weathering was reported to result in different distribution behavior compared to the virgin material [16,17].

Here, we report for the first time the laboratory use of low-density polyethylene (LDPE) plastic pellets (virgin material) as a low-cost, easy to reach and efficient sorbent material for extracting PAHs from environmental waters. The proposed methodology, termed plastic pellets sorptive extraction (P2SE), consists of a two-step procedure where target analytes are initially adsorbed onto the surface of three LDPE pellets and then desorbed using microliters of an organic solvent. Interphase mass transfer was greatly accelerated by means of vortex agitation. The proposed methodology was optimized, validated and applied to a variety of environmental waters as discussed in the following sections.

2. Experimental

2.1. Chemicals, materials and solutions

The three model PAHs compounds used here were naphthalene (Np), pyrene (Py) and benzo(a)pyrene (BaP). The octanol-water partition coefficients ($\log K_{ow}$) of these compounds ranged between 3.40 and 6.05. They were all purchased from Sigma–Aldrich (Steinheim, Germany) at a purity of >98%. Purified water was prepared from an EASYpure RF system (Barnstead/Thermolyne, IA, USA). All organic solvents were of pesticide grade. Sodium chloride (Merck, Darmstadt, Germany) was used to adjust the ionic strength of the aqueous samples. Stock solutions were prepared in acetone and stored at 4 °C in the dark when not in use. Working standards were prepared daily at the concentration level of interest.

LDPE, PP and polycaprolactam (Nylon 6) pellets were offered by local industrial plastic producers. The mean measured pellet mass ($n = 10$) was 23.0 ± 2.5 mg for PP and 10.5 ± 0.9 mg for Nylon 6. LDPE pellets with mass differences higher than 40% were discarded yielding a 27.3 ± 2.5 mg mean measured pellet mass. The mean measured pellet size ($n = 5$) was 3.9 × 4.6 × 3.0 mm (width x length x height) for LDPE, 3.5 × 4.6 × 2.9 mm (width x length x height) for PP and 2.9 × 2.2 mm (length x diameter) for the cylindrical Nylon 6 pellets. All pellets were cleaned by dipping them into different solvents (purified water, acetone, acetonitrile, 2-propanol, hexane and toluene) and sonicating the mixture for 10 min. Representative samples from each type of pellets were chemically desorbed using acetonitrile and the extract was analyzed using high performance liquid chromatography (HPLC) to ensure that they were free of contaminants. Although pellets were disposed after extraction, possible carry-over effects were evaluated by repeating the desorption step to three separate bathes of pellets previously used for P2SE of 20 mL aqueous samples spiked at 10 $\mu g\ L^{-1}$ with Np and 1.0 $\mu g\ L^{-1}$ with Py and BaP. Chromatographic analysis of the extracts yielded detectable amounts of analytes below the limits of quantification of the method.

Recovery studies were carried out using river water (collected from the Koiliaris River, located in Chania), wastewater effluent (collected from the municipal wastewater treatment plant of Chania serving approximately 70000 habitants) and seawater (collected from the beach of Nea Chora in Chania). Seawater samples collected in October and November from the harbor of Nea Chora in Chania were examined for possible PAHs contamination. The ionic strength of all real samples was adjusted to the optimum value (20% w:v NaCl) before extraction. All samples were collected the day before analysis and were stored in the dark at 4 °C.

2.2. P2SE procedure

P2SE is a two-step procedure comprising of an extraction and a desorption step. Unless otherwise stated within the text, a 20 mL spiked aqueous sample containing 20% w:v NaCl was placed in a 22 mL clear glass vial equipped with a screw cap and septum. Three LDPE pellets, selected to weight approximately 80 mg in total (mean measured mass of each set of three pellets 81.1 ± 1.3 mg ($n = 10$)), were then added and the mixture was vigorously shaken for 5 min at 3000 rpm (maximum setting) using a vortex agitator (VELP scientifica, Nemco, Europe). The LDPE pellets were then removed, dried with a lint-free tissue and transferred into a 1 mL

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