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A low-cost biosorbent-based coating for the highly sensitive determination of organochlorine pesticides by solid-phase microextraction and gas chromatography–electron capture detection

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ABSTRACT

In this study, an environmentally friendly and low-cost biosorbent coating was evaluated, for the first time, as the extraction phase for solid-phase microextraction (SPME) supported on a nitinol alloy. The characterization of the new fiber was performed by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA) and scanning electron microscopy (SEM). The applicability of the biosorbent-based fiber in the determination of δ -hexachlorocyclohexane, aldrin, heptachlor epoxide, α -endosulfan, endrin and 4,4'-DDD in water samples was verified, with separation/detection by gas chromatography coupled to electron capture detection (GC-ECD). The influencing parameters (temperature, extraction time and ionic strength) were optimized simultaneously using a central composite design. The optimum conditions were: extraction time of 80 min at 80 °C and sodium chloride concentration of 15% (w/v). Satisfactory analytical performance was achieved with limits of detection (LOD) between 0.19 and 0.71 ng L⁻¹ and limits of quantification (LOQ) between 0.65 and 2.38 ng L⁻¹. The relative recoveries for the analytes were determined using river and lake water samples spiked at different concentrations and ranged from 60% for α -endosulfan to 113% for δ -hexachlorocyclohexane, with relative standard deviations (RSD) lower than 21%. The fiber-to-fiber reproducibility (n = 3) was also evaluated and the RSD was lower than 14%. The extraction efficiency obtained for the proposed biosorbent coating was compared to a commercially available DVB/Car/PDMS coating. The proposed fiber provided very promising results, including LODs at the level of parts per trillion and highly satisfactory thermal and mechanical stability.

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1. Introduction

Sample preparation techniques have been widely used prior to applying analytical methodologies in order to perform the sample clean-up, concentrate analytes or transform the sample into a more suitable state for analysis, since with most instruments it is not possible to perform the direct analysis of complex sample matrices [1,2]. Recent trends have emphasized the importance of using a small amount of sample and a reduced volume of organic solvents, to encourage the use of environmentally friendly alternatives for the sample preparation step. Solid-phase microextraction (SPME)

is a solvent-free sample preparation technique and it represents an advance in that direction.

This technique, introduced in the 1990s by Pawliszyn and coworkers [3], combines the sampling, isolation and enrichment of the analytes in a single step, and represents an important development for the extraction of several organic pollutants at trace levels [4]. The advantages of using SPME include simplicity of operation, possibility of full automation, easy coupling with chromatography and faster extractions when compared to the classical extraction techniques [5,6]. SPME is based on the equilibrium of the partitioning of the analytes between the matrix and an extraction phase [5]. In its original form, SPME consists of a fused silica fiber coated with a thin layer of a suitable sorbent phase [7]. There are a number of commercially-available coatings for SPME and the extraction performance is dependent on the choice of an appropriate sorbent [8]. Despite the advantages of using SPME, some disadvantages are

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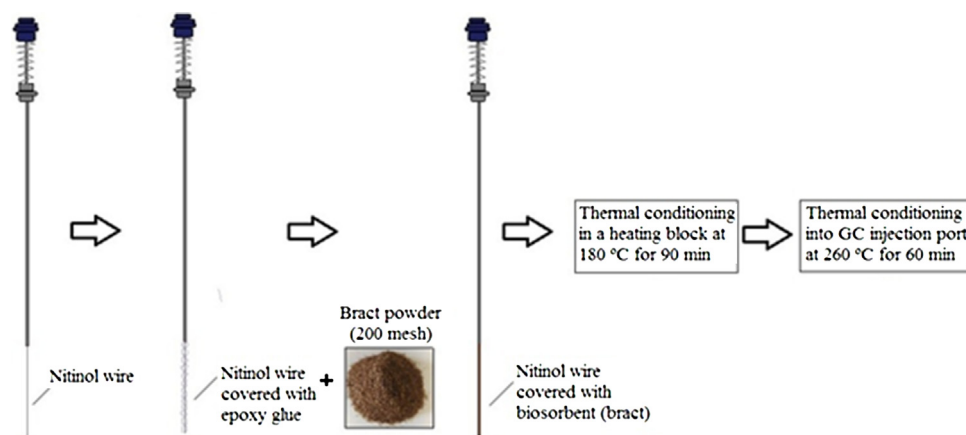


Fig. 1. Procedure for producing the biosorbent-based fiber.

associated with this technique including the fragility of the support (traditionally a fused-silica rod) and also the cost of commercial fibers is a drawback for some labs [9–11].

Considering the aforementioned issues, the development and application of new materials as supports and coatings for SPME are of great importance. Nitinol alloy (NiTi) has been reported as a promising alternative to replace fused silica support [12,13]. NiTi exhibits some advantages, including shape memory effect, superelasticity, durability, and wear and corrosion resistance [14]. Moreover, the development of different materials has provided a higher selectivity for specific compounds as well as low-cost analysis. Among these sorbent coatings, activated carbon [15,16], molecular imprinted polymers (MIP) [17–19], polymeric ionic liquids (PIL) [20,21] and nanomaterials [22,23] have been reported. Natural materials have also exhibited the potential for the use as sorbent phases in extraction/microextraction techniques. Biosorbents are formed by macromolecules containing a number of functional groups that are able to interact with compounds in different ways such as sorption, complexation and ion exchange. Lignocellulosic materials have been used as biosorbent for the determination of metals in biological and environmental matrices [24–26]. These materials are mainly comprised of cellulose and lignin, which are biopolymers with several polar and nonpolar chemical groups. Lignocellulosic materials offer a number of advantages when applied as extraction phases, including low-cost, high porosity, and easy availability [27]. Bracts, composed of a lignocellulosic material, are produced by the conifer tree *Araucaria angustifolia* (Bert) O. Kuntze, which is endemic in the south and southeast of Brazil and in eastern Argentina [28]. Most populations of *A. angustifolia* are located in the southern Brazilian states (Parana, Santa Catarina and Rio Grande do Sul) [29]. During flowering, *A. angustifolia* produces a cone of seeds, known as “pinhao” in Brazil. This is a dioecious species, i.e., male and female cones grow on separate trees. The female strobilus consists of pinhao seeds and bracts (non-developed seeds) [30]. Pinhao is generally cooked in boiling water and it is widely consumed in Brazil [31]. Bracts represent approximately 80% of the female strobilus, and they are usually discarded [30,31]. In the literature, investigations into the use of pinhao as a biosorbent to remove metals from aqueous solutions [28,31], or textile dye from aqueous effluents [32] have been reported. However, based on a literature search, the use of the bracts as a biosorbent for analytical applications does not seem to have been previously reported.

In this study, a novel proposal consisting of bracts as natural sorbent supported on a nitinol alloy as coating for SPME was investigated. The stability/applicability of this biosorbent was evaluated for the extraction of organochlorine pesticides (OCPs) from

water samples and determination by gas chromatography–electron capture detection. Although a large number of organochlorine pesticides have been banned, these compounds can be present in environmental water sources because of their physicochemical characteristics. For this study, multivariate optimizations were carried out and the analytical performance was examined by determining the analytical parameters of merit. In addition, the extraction efficiency obtained for the proposed coating was compared to a commercially-available SPME fiber. This novel approach increases the environmental-friendly aspect related to this sample preparation technique, since this biosorbent is natural, renewable and biodegradable.

2. Experimental

2.1. Reagents and materials

A standard solution of organochlorine pesticides containing a mix of δ -hexachlorocyclohexane, aldrin, heptachlor epoxide, α -endosulfan, endrin and 4,4'-DDD, in hexane:toluene (50:50 v/v) was obtained from Supelco (Bellefonte, PA, USA) at a concentration of 2000 $\mu\text{g mL}^{-1}$. From this standard, a stock solution was prepared in hexane (Sigma-Aldrich, Saint Louis, USA) at a concentration of 0.75 $\mu\text{g mL}^{-1}$ for each analyte, and stored at -4°C . For the optimizations and the evaluation of the analytical figures of merit (calibration curve, linear range, R, LOD and LOQ) the samples were prepared by adding the stock solution to ultrapure water obtained from a purification system (Mega Purity, Billerica, USA). The accuracy of the method was evaluated based on extractions using river water samples spiked with the analytes at three concentration levels and using lake samples spiked with the analytes. Sodium chloride (Synth, São Paulo, Brazil) was used to evaluate the influence of the ionic strength. A knife mill and a granulometric sieve with 200 mesh were used to prepare the bract powder. Nitinol wires with 0.2 mm of diameter and approximately 2 cm of length, epoxy glue (Brascola, São Bernardo do Campo, São Paulo, Brazil), sandpaper n. 600 (Carborundum, Rio de Janeiro, Brazil), and a heating block (Dist, Florianópolis, Santa Catarina, Brazil) were used for the fiber preparation. A thermostatic bath (Microquímica Ind. e Com. Ltda, Palhoça, Santa Catarina, Brazil), magnetic stirrers (Dist, Florianópolis, Santa Catarina, Brazil), magnetic stirrers obtained from Dist and 22 mL vials from Supelco were used. The real water samples were filtered through PTFE filters with 0.45 μm of pore size obtained from Allcrom (São Paulo, Brazil). A commercial fiber (DVB/Car/PDMS, 50/30 μm) obtained from Supelco was used to compare the efficiency in terms of the extraction of the OCPs compounds.

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