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A novel approach for electromembrane extraction based on the use of silver nanometallic-decorated hollow fibers

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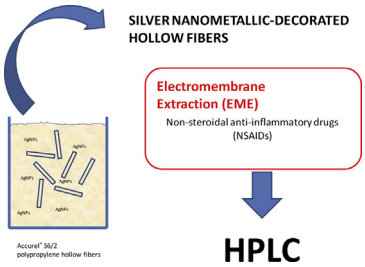
HIGHLIGHTS

- For the first time, a support containing metallic nanoparticles is used for EME.
- Polypropylene hollow fibers decorated with silver nanoparticles (AgNPs) were used as support.
- The presence of the NPs allows taking advantage of their singular properties.
- Procedure using the proposed support improves a previously published EME procedure for NSAIDs analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel approach based on the use of nanometallic-decorated hollow fibers to assist electromembrane extraction is proposed. Microporous polypropylene hollow fibers, on which nanometallic silver was deposited, have been used for the first time as liquid membrane support in electromembrane extraction (EME). Different methods for the generation/deposition of silver nanoparticles (AgNPs) were studied. The best results were obtained with chemical reduction of silver nitrate using $NaBH_4$ in aqueous solution followed by direct deposition on the hollow fibers. The extraction performance of the new supports was compared with a previously developed EME procedure used for the extraction of selected non-steroidal anti-inflammatory drugs (NSAIDs), resulting in an increase in the extraction ratio by a factor of 1.2–2 with a 30% reduction in the extraction time. The new nanometallic-decorated supports open new possibilities for EME due to the singular properties of nanometallic particles, including chemical fiber functionalization.

1. Introduction

Due to methodological, practical and environmental needs, traditional liquid–liquid extraction (LLE) procedures have evolved toward liquid phase microextraction (LPME) among other ones. LPME implies one or more transport steps through different organic or aqueous phases. Of all the different developed LPME

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methodologies, those that use supported liquid membranes (SLM) are the most widely used, essentially due to their robustness. The use of microporous polypropylene hollow fibers as liquid membrane support [1–3] has been the starting point for the development and widespread of the hollow fiber liquid phase microextraction (HF-LPME) techniques. Those are nowadays well established clean-up and preconcentration procedures for the determination of several analytes in all kinds of samples [4] and they are used as routine procedure in many analytical laboratories.

In 2006, Pedersen-Bjergaard and Rasmussen proposed a new microextraction procedure that was called electromembrane extraction (EME). The procedure, derived from three phase HF-LPME, consisted on the electrokinetic migration of the analytes through the SLM supported on microporous polypropylene hollow fibers by applying an electrical potential difference between both sides of the membrane [5,6]. Several EME procedures using flat membranes or hollow fibers have been developed for the determination of a wide variety of analytes [7]. These procedures present many advantages compared to three phase LPME ones.

Silver nanoparticles (AgNPs) have received considerable attention due to their attractive physical and chemical properties. They have a great interest in the field of medicine and biomedicine, as antivirals, fungicides or scarring agents [8–10]. The synthesis of nanoparticles in solution (colloidal solution) requires adequate methods to control the size and shape of the nanoparticles as well as obtaining a set of monodisperse particles. Silver nanoparticles can be synthesized using different methods: chemical reduction [8,9,11], electrochemical reduction[12], γ-irradiation [13] photochemical reduction [14,15], laser ablation [16], among others, being the most used the chemical reduction of silver salts by sodium borohydride.

On the other hand, recently, Hasheminasab et al. have proposed the use of dispersed multi-walled carbon nanotubes (MWCNTs) into the supported liquid membrane (SLM) on polypropylene hollow fibers Accurel® Q3/2 for EME purposes [17–19]. The MWCNTs dispersion in the SLM allows an additional adsorption/desorption process to the electrokinetic transport from the acceptor phase to the donor phase. Capillary electrophoresis was used for the determination of extracted basic (buprenorphine) [18] and acidic (ibuprofen and naproxen) [17] drugs and gas chromatography in a two-phase EME purpose for the determination of some basic drugs (tramadol and methadone) [19].

In this paper, we demonstrate for the first time that the use of microporous polypropylene hollow fibers decorated with silver nanoparticles allows to an increase in the extraction performance of EME devices. Six non-steroidal anti-inflammatory drugs (NSAIDs) were used as target analytes: salicylic acid (SAC), ketorolac (KTR), ketoprofen (KTP), naproxen (NAX), diclofenac (DIC) and ibuprofen (IBU). They were determined by HPLC using diode array and fluorescence detection in series mode.

Different ways of silver nanoparticles (AgNPs) generation/deposition were checked obtaining the best results using chemical reduction of silver nitrate in aqueous solution followed by direct deposition on the hollow fibers. Additionally, several tests to generate AgNPs directly on the fiber were also checked using sodium borohydride and/or UV radiation on silver impregnated hollow fibers.

The extraction performance of the new supports was compared with a previously developed EME procedure [20] used for the extraction of selected non-steroidal anti-inflammatory drugs (NSAIDs), showing the new proposed procedure increases in the extraction ratio by a factor of 1.2–2.

We have developed a novel alternative with the aim of improving EME procedures in terms of enrichment factors and time of analysis. The modification of the external and porous surface of the hollow fiber, by depositing metallic nanoparticles, helps to increase the electrokinetic transport efficiency, as well as, will allow the use of a wider variety of organic solvents as supported liquid membranes and, additionally, due to the singular properties of nanometallic particles such specific interactions with selected organic functional groups and electrical behavior, will make the fiber usable for specific purposes.

2. Experimental

2.1. Chemicals and reagents

All chemicals were of analytical-reagent grade. Salicylic acid (SAC), ketorolac (KTR), ketoprofen (KTP), naproxen (NAX), diclofenac (DIC), ibuprofen (IBU), silver nitrate, sodium borohydride, ascorbic acid, and citric acid were obtained from VWR (Barcelona, Spain) and 1-octanol was purchased from Fluka–Sigma–Aldrich (Madrid, Spain).

All solutions and dilutions were prepared using ultrapure water from a Milli-Q Plus water purification system (Millipore, Billerica, MA, USA). Aqueous working solutions of NSAIDs were daily prepared by adequate dilutions from methanolic (KTP, NAX) and aqueous (SAC, KTR, DIC, IBU) 100 mg L^{-1} stock solutions.

2.2. Synthesis of AgNPs

Synthesis of AgNPs was based on the method described by Solomon et al. [21] in which ionic silver was reduced and then nanoparticles formed were stabilized with sodium borohydride. 10 mL of 1.0 mM silver nitrate was added dropwise and slowly (about 1–2 drops s^{-1}) to 30 mL of 2.0 mM sodium borohydride solution that was vigorously stirring on a magnetic stir plate and chilled in an ice bath. The solution turned from light yellow after the addition of 2 mL of silver nitrate to bright yellow when all of the silver nitrate has been added. The process took about 3 min. Stirring was stopped and the stir bar removed.

The synthesized AgNPs were characterized by UV–vis absorption spectroscopy showing the obtained solution a characteristic surface plasmon resonance at 391 nm that corresponds to AgNPs lower than 40 nm [22]. The AgNPs solution remains stable at least for two weeks (4 °C).

2.3. Preparation of silver nanometallic-decorated hollow fibers

Accurel® S6/2 polypropylene hollow fibers (1800 μm i.d., 450 μm wall thickness and 0.2 μm pore size) from Membrana (Wuppertal, Germany) were cut into 25 mm pieces, washed with acetone in an ultrasonic bath and dried; the fiber was closed in the lower end by thermal and mechanical pressure. The fiber pieces were immersed in the sodium borohydride solution during silver nanoparticles synthesis and maintained immersed for 5 min. Hollow fibers were then takeout and 1 mL of the synthesized solution of nanoparticles was introduced through the pores by pressure using a medical syringe. Finally, the fibers were slowly washed with water and air dried in darkness. Prepared silver nanometallic-decorated hollow fibers can be used at least for three weeks.

2.4. Proposed EME procedure

The electrical equipment consisted in a d.c. power supply model Power Source 300 V (VWR International, Barcelona, Spain) with programmable voltage in the range 2–300 V, providing currents in the range 4–500 mA. Simple platinum wires (0.5 mm diameter) electrodes were introduced in the sample and acceptor solutions with an average inter-electrode distance of 2 mm resulting an average electrical field of 50 V cm^{-1} (for a typical 10 V d.c.). 10 mL