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Dispersive micro-solid phase extraction of bisphenol A from milk using magnetic nylon 6 composite and its final determination by HPLC-UV

Emilia M. Reyes-Gallardo, R. Lucena, S. Cárdenas, M. Valcárcel *

Department of Analytical Chemistry, Institute of Fine Chemistry and Nanochemistry, Marie Curie Building, Campus of Rabanales, University of Córdoba, 14071 Córdoba, Spain.

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ABSTRACT

Herein, a new method for the determination of bisphenol A (BPA) in milk samples is presented. This method comprises a precipitation process, bearing in mind that the analyte has a high tendency to interact with the fatty compounds of the milk, and a magnetic micro-solid phase extraction prior to the determination by high-performance liquid chromatography with UV detection. The presented precipitation process combines EDTA-McIlvaine buffer (the common precipitation agent) with acetonitrile to facilitate the transference of the analyte to the supernatant (only the 30% is transferred in the absence of acetonitrile). The employed sorbent, a magnetic nanoparticles-nylon 6 composite, was synthesized in a quick and one-step method, and was also characterized by several instrumental techniques (SEM, TEM, FT-IR, and SQUID). The developed methodology provides a limit of detection of 3.05 μg/L, which is in accordance with the specific migration limit (SML) established by the European Union. The repeatability of the method, in terms of relative standard deviation, was better than 9.1% (at 100 μg/L) and 16.8% (at 25 μg/L). The recovery study provided values in the range from 86 ± 7 to 99 ± 5%.

1. Introduction

Bisphenol A (BPA), 4,4′-(propane-2,2-diyl)diphenol, is an estrogenic endocrine-disrupting monomer which is extensively used in the plastic industry. BPA is mainly employed for two different purposes: a) as a monomer in the fabrication of polycarbonate plastic products and epoxy resins, and b) as an additive in polyvinyl chloride plastics and other products (for example, flame retardants) [1]. Although only a little percentage of these plastics is applied in the food and beverage containers industry, contaminated food intake is the major source (ca. 90%) of the overall BPA exposure [2]. The thermal treatment of these containers, that favors the leaching of BPA into food, is the reason behind that situation [3].

BPA has been determined in a variety of biological and food samples, including human colostrums [4], breast milk [5], water [6], soft drinks [7], and canned food [8], among others. Due to its potential risk, in 2002, the European Union established the specific migration level in food at 3 mg/kg, although this value was finally amended to a value of 0.6 mg/kg [9]. According to this legislation, the determination of BPA in cow milk, a usual commodity, is desirable. However, this determination is not simple due to the complexity of the sample. In fact, the fatty content of milk, which varies between 0.3 and 4% depending on the type (whole, defatted or skim), makes the BPA determination a real challenge since BPA tends to interact with the fat (due to its hydrophobic nature) making the sample matrix–analyte interaction more intense. This interaction still remains even during the precipitation process that is usually employed as milk pretreatment in analytical methodologies [10].

Several extraction techniques have been proposed for the isolation/preconcentration of BPA from milk sample including solid phase extraction (SPE) [11], solid-phase microextraction (SPME) [12,13], molecularly imprinted SPE [6,14,15], or immunoaffinity chromatography [8].

The use of nanoparticles (NPs) in the microextraction context has improved the performance of the developed techniques. The larger superficial area of NPs (that enhances the extraction kinetic) and the variety of different interaction chemistries (that makes wider the applicability to different problems) can be considered among the main reasons. The combination of different types of NPs (hybrid NPs) as well as the combination of NPs with micrometric systems (composites) has increased the potential of this type of materials in analytical sciences. Within the composites, the combination of magnetic nanoparticles (MNPs) with micrometric polymers is especially interesting. In this sense, the composite presents high extraction capabilities due to the polymeric network while maintains a magnetic behavior that simplifies the overall extraction procedure [16].

Polyamide polymers, including nylon-6, are interesting sorbents that can be easily synthesized in the laboratory using common reagents. Polyamides present inter- and intra-molecular hydrogen bounds through their amide groups that allow the stacking of the linear polymer chains. These bounds may be developed with external carbonyl or amine groups permitting the interaction with target molecules [17].

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* Corresponding author. Tel./fax: +34 957 218 616.
E-mail address: qa1meobj@uco.es (M. Valcárcel).

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In addition, non-polar interactions with the hydrocarbon polymer chain are also possible, increasing the versatility of the polymer. Taking this into account, polyamides have been previously reported for the extraction of BPA in water samples, using microfiltration membranes [18]. Here, the use of magnetic NPs-nylon 6 composite is proposed instead of membranes in order to obtain a better dispersion of the sorbent and to avoid the sealing of the membranes when using complex samples as milk. The synthesis of the composite is very simple, as it can be achieved by a simple solvent changeover [19].

In this article, a magnetic NPs-nylon 6 composite is employed for the dispersive micro-solid phase extraction (d-μSPE) of BPA from milk samples, the analyte being finally determined by HPLC-UV. The main aim is to provide a method, giving priority to simplicity over sensitivity, to fulfill the SML established by the EU legislation.

2. Experimental section

2.1. Reagents

All reagents were of analytical grade or better. Bisphenol A was purchased from Sigma–Aldrich (Madrid, Spain). A stock standard solution of the analyte was prepared at a concentration of 400 mg/L in methanol (Carlo Erba Reagents, Italy) and stored at 4 °C. Working solutions were daily prepared by the appropriate dilution of the stocks in Milli-Q water (Millipore Corp., Madrid, Spain).

Iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), iron (II) chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$), and ammonia were used for the synthesis of the magnetic nanoparticles (Fe_3O_4). Tetraethylorthosilicate (TEOS) and ethanol were employed for covering the NPs with a protective silica-based coating. Formic acid and nylon 6 were used for the preparation of the polymer network where the MNPs are embedded. Sodium phosphate dibasic dihydrate, citric acid monohydrate, and ethylenediaminetetraacetic acid(EDTA) were employed for the preparation of EDTA–McIlvaine buffer. All these reagents were purchased from Sigma–Aldrich.

EDTA–McIlvaine buffer solution (pH = 4) was prepared by dissolving 7.5 g of disodium hydrogen phosphate, 6.5 g of citric acid, and 1.86 g of EDTA in 500 mL of water.

Whole, defatted, and skim milk samples were purchased from local markets and were maintained in their own containers under normal storage conditions.

2.2. Synthesis of the magnetic nanoparticles-nylon 6 composite

The synthesis of the magnetic nylon 6 composite is described elsewhere [19], and it consists of different steps. In brief, Fe_3O_4 MNPs are synthesized by a coprecipitation method and coated with a silica shell ($Fe_3O_4@SiO_2$) [20] using TEOS as reagent. The magnetic nylon 6 composite was finally synthesized as follows: 150 mg of nylon-6 were dissolved in 5 mL of formic acid and then 200 mg of $Fe_3O_4@SiO_2$ were dispersed into the solution. After that, the dispersion was injected with a syringe into a beaker with water, to cause the gelation of the nylon-6 around the magnetic NPs. The gelation is produced by solvent changeover since nylon is soluble in formic acid but it is insoluble in water. The solid was washed, recovered using an external magnet, and finally dried.

2.3. Apparatus

Liquid chromatographic analyses of bisphenol A were performed using an Agilent 1100-system liquid chromatograph (Agilent®, Palo Alto, CA) equipped with a binary high-pressure pump 1200 series), a single wavelength photometer (1100 series), and an autosampler. Data analysis was carried out using HP ChemStation software. Chromatographic separations were developed on a LiChrosorb® C18 column (5 μm, 4.6 × 250 mm) (AnálisisVínicos, Tomelloso, Spain) under an isocratic program using 65% of acetonitrile (solvent B) and 35% of water (solvent A) as mobile phase components. The flow rate was set at 1 mL/min, the injection volume was 10 μL, and the analyte was monitored at 226 nm.

For the synthesis of the composite, a heating magnetic stirrer (VelpScientifica®,Milan, Italy) was used. A test tube shaker (Reaxtop^{TM} Heidolph, Schwabach, Germany) and an ultrasonic bath (model 3510, Branson®, Danbury, CT, USA) were employed in the extraction procedure. A centrifuge (model Centronic BL-II^{TM}, J.P. Selecta, Barcelona, Spain) was used during milk samples pretreatment and a vacuum concentrator (Eppendorf Concentrator plus^{TM}, Eppendorf, Germany) was employed to evaporate the obtained extracts.

An external magnet (60 × 30 × 15 mm and 549.4 N of maximum magnetic force), purchased from Supermagnete (Gottmadingen, Germany), was employed for the sorbent recovery after D-μSPE.

2.4. Characterization of the magnetic nanoparticles-nylon 6 composite

Micrographs of the NPs were obtained in a Philips® CM-10 transmission electron microscopy (TEM) and a JEOL® JSM 6300 scanning electron microscopy (SEM).

Infrared measurements 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 600 cm^{-1} at a 4 cm^{-1} resolution with 64 coadded scans each. Data collection was made using OPUS software (version 4.2) (Bruker, Ettligen, Germany).

Magnetic behavior was analyzed performing a hysteresis loop using a Superconducting Quantum Interference Device (SQUID) MPMS-XL-7 T from Quantum Designs® (San Diego, CA, USA) at constant temperature (27 °C).

2.5. Sample extraction procedure

The extraction procedure of the milk samples involves several steps. First of all, milk samples are pretreated to induce protein precipitation. For this purpose, 20 mL of sample are mixed with the same volume of EDTA–McIlvaine buffer/acetonitrile solution (20/80, v/v) obtaining a final concentration of ACN of 40%. This medium is left to stand for 1 h and centrifuged (8000 rpm or 6439 *g*, 9 min). Then, 10 mL of the supernatant are four-fold diluted with McIlvaine buffer, and 80 mg of the composite are added subsequently to this medium. The sample is stirred in a test tube shaker for 1 min and sonicated for 30 min to favor the extraction of the analyte. After that, the sorbent is isolated from the sample by an external magnet and washed with 10 mL of milli-Q water. Once the sorbent is completely dried, the analyte is batch-mode eluted using 500 μL of methanol. After that, the liquid is recovered after the magnetic separation of the solid. To improve the sensitivity, the extract is evaporated to dryness in a vacuum concentrator and redissolved in 50 μL of methanol before the final HPLC analysis.

Due to its easy and cheap synthesis, a fresh amount of composite is employed for each extraction avoiding potential carry-over effects.

3. Results and discussion

3.1. Characterization of the magnetic nanoparticles-nylon 6 composite

The synthesized composite was characterized by SEM, TEM, FT-IR, and SQUID. SEM micrographs (Fig. 1A) show that the surface of the polymer becomes rougher after the synthesis. According to TEM images (Fig. 1B), the MNPs are spherical and have an average diameter of 10 nm.

FT-IR was used to confirm the chemical composition of the composite (Fig. 2). A characteristic band at 580 cm^{-1}, which can be assigned to the Fe—O—Fe vibration, can be observed. The Si—O—H and Si—O—Si

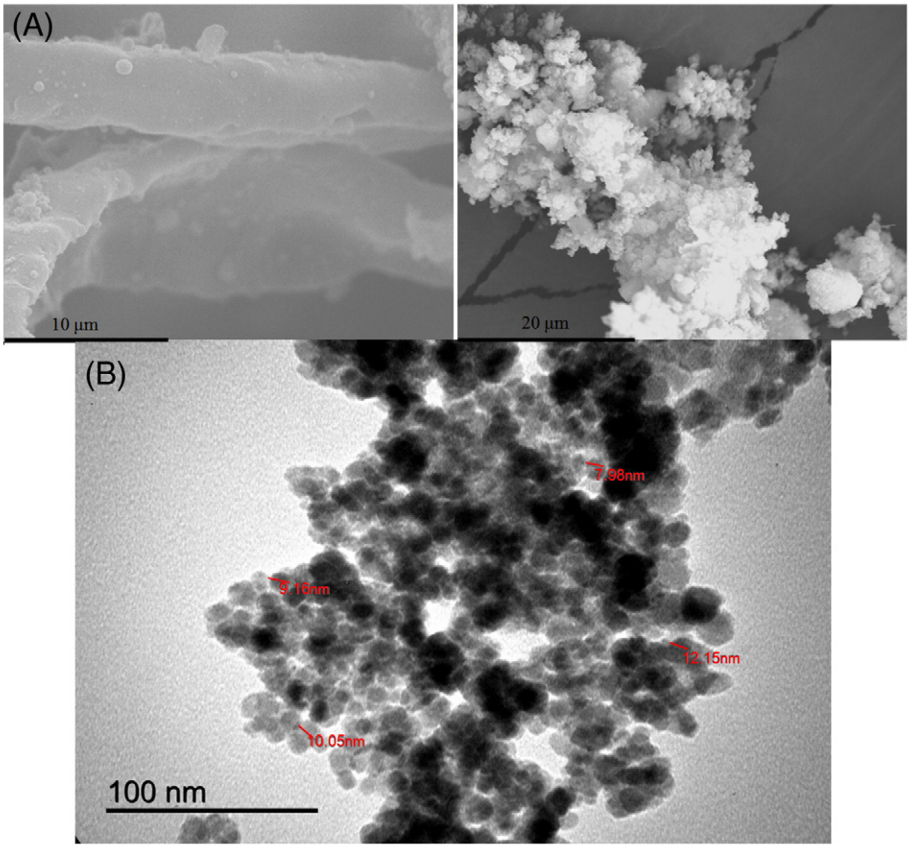

Fig. 1. (A) Scanning electron microscopy (SEM) images of nylon 6 (left) and magnetic nanoparticles-nylon 6 composites (right). (B) Transmission electron microscopy (TEM) images of magnetic nanoparticles-nylon 6 composite.

bonds present a strong absorbing region at 1200–1000 cm^{-1}. The presence of nylon in the structure involves the appearance of a band around 1642 cm^{-1} (the C═O stretching of the amide group) and another band around 1546 cm^{-1} (the N—H deformation of the amide I).

The magnetic behavior of the synthesized sorbent is key for the development of efficient and fast procedures. The saturation magnetization of the composite was investigated by magnetic hysteresis loop analysis (Fig. 3). The symmetrical shape of the curve suggests that there is no magnetic retentivity and therefore the composite shows superparamagnetism, obtaining a saturation magnetization value bigger than 40 emu/g. This value is much higher than other hybrid polymeric materials previously synthesized [21] and allows the easy and fast separation of the sorbent.

3.2. Sample pretreatment optimization

Protein precipitation is required to perform an efficient extraction protocol of milk samples. This precipitation, which can be performed using different alternatives (pH change, the addition of organic solvents, or the modification of the ionic strength), produces a protein clot where the fatty compounds of the milk are trapped [10]. Due to its hydrophobicity, bisphenol A presents a high tendency to interact with the fat and its transference to the supernatant might be compromised.

Taking this into account, the precipitation method should be optimized. Whole milk, due to its higher fat percentage, was employed

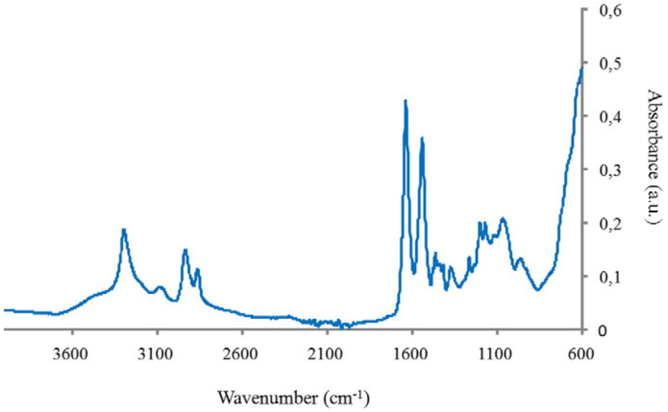

Fig. 2. Infrared spectrum of magnetic nanoparticles-nylon 6 composite.

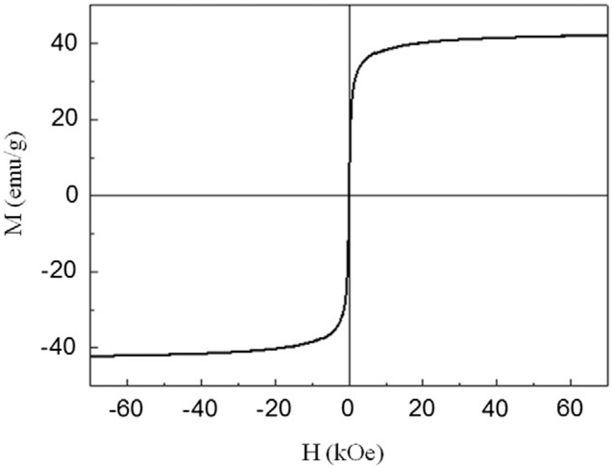

Fig. 3. Magnetization curve of the MNPs-nylon 6 composite at 27 °C.

as model sample. The use of EDTA–McIlvaine buffer, which is the common precipitation reagent, did not produce good results. Different buffer/sample ratios (Fig. 4A) were tested but only the 30% of the original BPA was transferred to the supernatant due to the strong retention of BPA in the protein/fat clot.

In order to increase this transference, acetonitrile was added to the buffer. The effect of the acetonitrile in the transference efficiency was evaluated in the following way. 5 mL of spiked whole milk (4 mg/L was used in order to measure the analyte without any preconcentration step) were deproteinized with 5 mL of a mixture of buffer and acetonitrile with different proportions and the supernatants were directly analyzed. According to the results, which are summarized in Fig. 4B, the transfer of the analyte increases with the acetonitrile percentage, the maximum value being obtained at 40% of the total volume. Under these conditions, the analyte is quantitatively transferred to the liquid phase. Higher acetonitrile concentrations were not evaluated since it negatively affects to the subsequent D-μSPE procedure increasing the analyte solubility in the liquid phase. To study this influence, several standards containing the analyte at the equivalent concentration (2 mg/L) were prepared in different McIlvaine buffer/acetonitrile proportions and extracted with 5 mg of the composite. All the standards were analyzed before and after the extraction process to calculate the analyte extraction recovery. The results, which are shown in Fig. 4C, corroborate the negative effect of acetonitrile in the transference of the analyte from the supernatant to the composite. To make compatible the milk extract with the subsequent D-μSPE, the precipitation extract was 4-fold diluted with buffer before the addition of the composite. In this way, the acetonitrile percentage is reduced from 40% (its concentration in the precipitation medium) to 10%, making possible the retention of the analyte on the composite.

3.3. D-μSPE optimization

The effect of several variables on the extraction of the BPA from milk was then considered in depth. All variables were evaluated using blank whole milk samples spiked with the analyte at a concentration of 500 μg/L. This concentration level was employed taking into account the legal SML and to avoid the saturation of the sorbent when real samples are processed. Before processing the spiked samples, they were pretreated following the optimum protein precipitation protocol previously described. To begin with the optimization, 30 min were fixed at the extraction time and the elution step was carried out with 500 μL of methanol, being the extract evaporated to dryness and the residue redissolved in 50 μL of methanol.

Sorbent amount and sample volume were studied jointly since they are directly related. Sample volume was optimized in the range from 1 to 10 mL, and sorbent amount between 20 and 80 mg, the result being shown in Fig. 5. The analyte signal increased with both the sorbent amount and the sample volume as it was expected. The maximum signal was obtained for 5 mL of sample (which corresponds to a final extract volume of 40 mL) and 80 mg of sorbent and therefore these conditions were selected for further analyses.

Extraction time was evaluated in the range from 5 to 60 min. The results showed that the signal of the analyte increased with the extraction time up to 30 min, after that, the signal remained constant.

3.4. Analytical figures of merit and sample analysis

The calibration graph for BPA was built by extracting several blank samples spiked with the analyte in the range from 10.2 μg/L to 4 mg/L, a good linearity ($R > 0.996$; $S_{y/x} = 5.6$; MAD $= 39$) was observed. The sensitivity of the method was evaluated according to the limit of

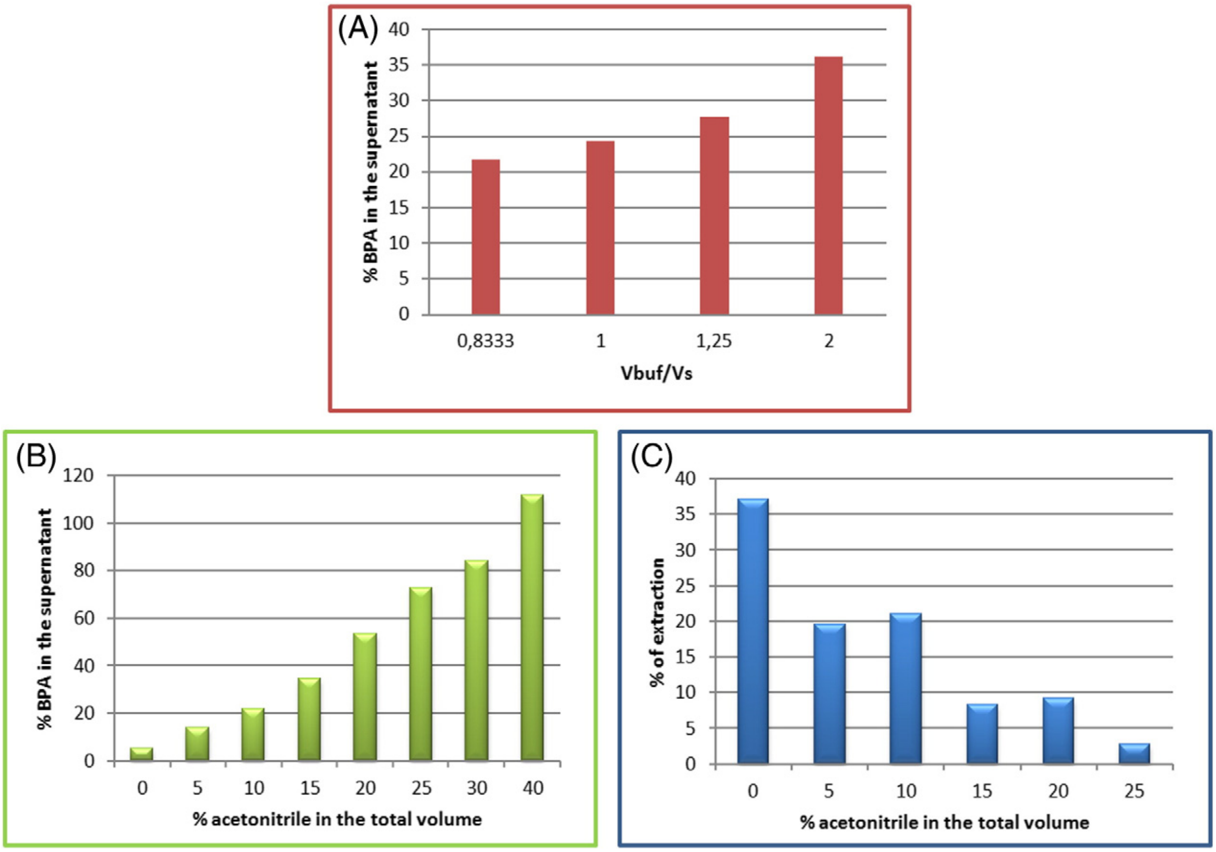

Fig. 4. (A) Evaluation of the buffer/sample ratio (V_{buf}/V_s) for the transfer of the target analyte to the supernatant. (B) Evaluation of the percentage of acetonitrile in the transfer of the analyte. (C) Evaluation of the percentage of acetonitrile in the extraction of the analyte.

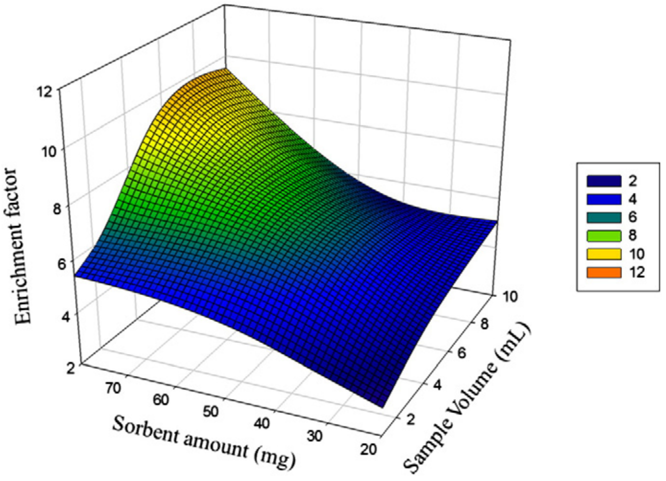

Fig. 5. Effect of the sample volume and the sorbent amount on the extraction of the target analyte.

detection (LOD). The LOD, which was calculated by using a signal-to-noise ratio of 3, was 3.05 μg/L. The limit of quantification (LOQ), for a signal-to-noise ratio of 10, was 10.16 μg/L. The repeatability of the method, in terms of relative standard deviation (RSD, %), was evaluated in septuplicate at two different concentration levels: 100 μg/L and a concentration closer to the limit of quantification (25 μg/L). The results were 9.1% and 16.8%, respectively. Inter-day precision was also estimated at 100 μg/L over 3 days ($n = 9$), obtaining a RSD of 9.5%. These precision values involve also the synthesis reproducibility since 80 mg of fresh composite are used for each new extraction while the amount of composite synthesized per batch is ca. 300 mg.

The enrichment factor, which was obtained by comparing the calibration graphs before and after the extraction process, was 7.58 and the absolute extraction recovery, which refers to the percentage of total analyte that can be extracted efficiently by the sorbent and finally eluted with methanol in the fortified whole milk samples, was 7.58%. The EF is not too high due to the coexistence of two subsequent steps (precipitation and extraction) where the addition of acetonitrile plays an opposite effect.

The performance of the method was evaluated through the analysis of different kinds of milk samples including whole, defatted, and skim. Since no sample contained the analyte in a measurable concentration, a recovery study was performed spiking the samples with the analyte at 100 μg/L. The relative extraction recoveries (expressed as percentages with standard deviations) were 86 ± 7, 98 ± 4, and 99 ± 5% for whole, semi-skimmed, and skimmed milk, respectively, satisfying all of them the 70–130% recovery criterion. The increase in the percentage of extraction is directly related with the amount of fat that is contained in the sample since BPA is strongly retained in the protein/fat clot.

4. Conclusions

In this paper, an estrogenic endocrine-disrupting monomer, bisphenol A, is determined in different kind of milk samples (whole, defatted, and skim). The extraction procedure is carried out using a magnetic-nylon 6 composite in a dispersive micro-solid phase extraction format, the analyte being finally determined by HPLC-UV. Table 1 presents a comparison of the proposed method with other counterparts based in non-sophisticated instrumental techniques such as HPLC-UV or HPLC-FD [6,12–15]. The proposal extraction method provides the higher LOD although it requires a lower sample amount. However, it is suitable to detect BPA below the SML established by the European Union (600 μg/kg) although BPA can be found in real samples at lower concentrations. The precision is in the same order of magnitude of several approaches [6,14,15] although it is surpassed by the SPME approaches [12,13] due to the potential automation of the latter. Finally, it provides very good recoveries when real samples are processed.

The main advantage of the technique is the simplicity of the sorbent obtaining over MIPs synthesis [6,14,15]. The composite can be obtained in a simple, quick, and one-step method using commercially available polymers.

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Table 1

Comparison of the proposed method with other counterparts using non-sophisticated instrumental techniques.

Instrumental technique	Sample treatment	Sample amount	LOD (μg/L)	Precision (% RSD)	Relative recovery (%)	Reference
HPLC-UV	MIP-SPE	50 mL	0.16 μg/L	6.1–10.5	95–101	[6]
HPLC-DAD	SPME using polymeric ionic liquids	20 mL	0.09 μg/L	<4.69	74.8–107	[12]
HPLC-FD	SPME	10 mL	0.2 μg/L	6.6	93–102	[13]
HPLC-FD	Magnetic MIP-SPE	20 mL	0.3 μg/L	8.9–12.6	72–113	[14]
HPLC-FD	MIP-SPE	5 g	1.32 μg/kg	12–14	86–111	[15]
HPLC-UV	Magnetic SPE	5 mL	3.05 μg/L	9.1–16%	86–99	This work

HPLC, high-performance liquid chromatography; UV, ultraviolet detection; DAD, diode array detection; FD, fluorescence detection; MIP, molecularly imprinted polymer; SPE, solid phase extraction; SPME, solid phase microextraction; LOD, limit of detection; RSD, relative standard deviation.

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